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Ordered alloy formation for Pt₃Fe/C, PtFe/C and Pt_{5.75}Fe_{5.75}Cu_y/C O₂-reduction electrocatalysts

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Abstract

Carbon supported Pt₃Fe, PtFe and Pt_{5 75}Fe_{5 75}Cu catalysts are prepared via the impregnation of Fe and/or Cu-nitrate precursor salts onto a preformed nano-sized Pt/C catalyst. They are referred to as Pt₃Fe/C, PtFe/C and Pt_{5.75}Fe_{5.75}Cu/C catalysts and the subscripts refer to the nominal Pt, Fe and Cu atomic ratios. The final catalysts are obtained by annealing the impregnated samples in a H₂ enriched atmosphere. Pt_{5.75}Fe_{6.75}/C, Pt_{5.75}Cu_{6.75}/C and Pt_{5.75}Fe_{5.75}Cu₂/C catalysts were also made. The as-prepared catalysts are characterized using X-ray diffraction, transmission electron microscopy, standard electrochemical methods and probed for the electrochemical O₂ reduction reaction (orr). Rietveld analyses reveals that [Fm-3m] Pt, cubic [Pm-3m] Pt₃Fe and tetragonal [P4/mmm] PtFe structure types are made. In case of the Pt_{5.75}Fe_{5.75}Cu/C catalyst, a nano-sized carbon-supported single-phase catalyst of [P4/mmm] structure is found to be made at 800 °C, with Pt and Fe ordered on separate lattice planes, while Cu is distributed randomly onto both Pt and Fe atomic planes. The PtFe/C equivalent catalyst contains in addition a separate Fe phase as well as a slightly disordered [P4/mmm] phase. Pt_{5 75}Cu_{6 75}/C forms a disordered cubic [Fm-3m] alloy structure. The activity towards the orr was measured after 70 potential cycling, which can cause beneficial changes to the catalysts. In case of the specific orr activity, a dependence on the catalyst series is observed as follows: Pt_{5.75}Fe_{5.75}Cu/C [P4/mmm] > PtFe/C [P4/mmm] > Pt₃Fe/C $[Pm-3m] \approx Pt_{5.75}Cu_{6.75}/C$ [Fm-3m] > Pt/C [Fm-3m]. The highest orr mass activities are also found for the Pt_{5.75}Fe_{5.75}Cu/C and subsequently for the PtFe/C catalysts. Estimated orr activities are well within the range reported in the literature. In fact the specific orr activities compare to results reported for so called de-alloyed catalyst that are among the highest orr mass activities reported in the recent literature.

1. Introduction

Polymer electrolyte fuel cells (PEMFCs) have attracted a lot of attention due to their potential use as power sources for automotive and stationary applications [1,2]. However, there are still substantial hurdles that need to be overcome before these devices can be considered as viable technologies. It is known that the lifetimes of the catalysts, the membrane and the catalyst supports need to be prolonged for practical PEMFC applications. An important goal for automotive applications is to reduce the amount of Pt presently used as the O_2 reduction (orr) catalyst. This is considered essential in order to make PEMFCs economically viable.

Various Pt based alloys have been explored for decades with the goal to achieve high orr activities [2-11]. Other catalyst architectures referred to as core-shell, surface strained and Pt enriched catalysts have also been suggested [6,7,12-17]. Increases in mass and specific orr activities of such catalysts over Pt-only catalysts have been reported. However, the reported orr activities can vary widely. Nevertheless, it has been established that Pt alloys can show higher specific as well as mass orr activities than Pt-only catalysts [2,5,6,9]. Very large increases in specific orr activities of up to 10 and 90 times have been reported for bulk alloy catalysts consisting of a surface enriched with Pt or a monolayer of Pt [15]. However, in order to achieve sufficiently high mass orr activities, practical catalysts are of 4-5 nm average size rather than of bulk metal dimensions. There are also reports of catalysts that consist of a monolayer of Pt on Pd core nano-particles [18]. This appears to be the only proven nano-sized Pt monolayer system. In fact, the engineering of a Pt monolayer on a foreign metal or alloy of less than 5 nm is a challenge and has to the best of our knowledge not yet been achieved, except for the case of utilizing Pd as a core. However, Pd is relatively expensive. Furthermore, under FC operating conditions, Pd will become exposed once the Pt starts to dissolve. Pd is unstable in acidic media when exposed to high potential excursions.

It is generally accepted that the increase in the specific orr activity of Pt-alloy vs. Pt-only catalysts is linked to a compression of the Pt lattice [3-5]. Similarly, reported enhancements in the orr activity of originally called Pt "skeleton", then "surface strained" or "core-shell type" catalysts have been assigned to a lowering of the Pt-Pt bond distance [16,17]. Electronic effects have also been suggested to be of benefit for the orr activity. The latter is related to the reduction in the d band character [19]. This, in turn, is believed to weaken the Pt-O bonding, thus exposing a larger fraction of the Pt as Pt-metal. Pt-metal is the effective catalyst for the orr. The structure

of the Pt-alloy catalysts likely also influences the orr activity. Ordered catalysts have been reported to show improved activities [12,20]. Other results report high activities for so-called surface strained catalysts produced by electrochemical de-alloying [16]. It is known that the final catalyst structure depends on many factors such as the composition and the temperature used for the preparation as well as the Pt/C precursor and catalyst support. Catalysts composed of Pt_xFe_y and $(PtFe)_xCu_y$ may make interesting test systems. Pt_xFe_y/C catalysts have shown enhanced orr activities over other Pt based catalysts [6,10], and the Pt_x plus Fe_y system has the potential to form a variety of alloy structures [21]. Research, carried out on thin films, has further shown that the combination of Pt, Fe and small amounts of Cu allows for the formation of an ordered alloy phase at lower annealing temperatures than observed for Pt and Fe only [22,23]. Therefore, the addition of a small amount of Cu to Pt and Fe may allow for the preparation of well defined, and perhaps single phase alloys catalysts in the nano-size range on carbon supports at lower temperatures than for Cu-free catalysts. Pt_xFe_yCu_z electro-catalysts for the orr have been reported previously [24]. However, the previous reports did not provide a study of the influence of the addition of Cu to the catalysts, i.e., comparing Pt_xFe_yCu_z vs. Pt_xFe_y type catalysts, which is the object of this study.

In this work, various $Pt_xFe_yCu_z/C$ catalysts are prepared using a wet impregnation method and annealing in a H₂ enriched atmosphere between 250 and 800 °C. The preparation involves the impregnation of appropriate amounts of Fe and/or Cu-precursor salts onto a home-made Pt/C catalyst. The as-prepared catalysts are characterized using XRD, TEM, EDS and standard electrochemical methods. The orr activities of these catalysts are measured and compared to three Pt/C catalysts. It should be noted that the main concern of the present study is to establish synthesis conditions that allow for the preparation of specific catalyst structures, which, in turn, can be used to probe the orr activity. Concerns like a potential negative impact of dissolved Fe and Cu onto the membrane electrode assembly and anode catalyst are not discussed in this study.

2. Experimental

2.1 Preparation of the catalystsPt/C precursor: All catalysts made in this work are supported on Vulcan XC-72R (Cabot). A well defined 20 wt.% Pt/C precursor powder of 2.1 (±1) nm Pt size was first made using a literature method [23] and used as starting material for the

preparation of the binary and ternary catalysts. The Pt/C precursor catalyst was made by depositing a specific volume of a colloidal Pt solution onto Vulcan XC-72R. The Pt colloids were synthesized by first dissolving 0.4652 g PtCl₄ (Alfa Aesar, 99.9% metal basis) in 50 mL of ethylene glycol (EM Science) containing 0.15 M NaOH. The pH of the synthesis solution defines the resulting particle size of the Pt colloids, as discussed in previous work [25,26]. The solution was stirred for 1 h at room temperature, and subsequently heated under reflux at 160 °C for 3 h. A dark brown colloidal Pt solution was formed in this manner, which was allowed to cool in air and room temperature for 1 h, before it was mixed with 1.077 g Vulcan XC-72R in a beaker and allowed to stir for 24 h. Appropriate amounts of 1 M HNO₃ were added to adjust the pH to 2 allowing for complete deposition of the Pt colloids onto the carbon support [26]. After 24 h, the Pt/C powder was filtered and extensively washed with water and ethanol. A clear filtrate was obtained indicating that the Pt colloids were completely deposited onto the carbon support. The powder was then dried in an air oven at 80 °C over night, and subsequently homogenized in a glass mortar.

Pt₃Fe/C, PtFe/C, Pt_{5.75}Fe_{6.75}/C, Pt_{5.75}Fe_{5.75}Cu/C, Pt_{5.75}Fe_{5.75}Cu₂/C and Pt_{5.75}Cu_{6.75}/C catalysts: Various Pt-alloy catalysts were prepared by ultrasonically dispersing 500 mg of the Pt/C precursor powder in 120 mL of water in a 250 mL beaker for 1.5 h. Fe(NO₃)₃·9H₂O (Alfa Aesar, 99.99% Fe basis) and/or Cu(NO₃)₂·6H₂O (Acros organics) were used as precursor salts. Appropriate amounts of the precursor salts were added to the suspension, as listed in Table 1. Upon dissolution of the precursor salts the pH of the suspension was adjusted to 4 by adding a few drops of 1 M HNO₃ to assist in the dissolution of the precursor salts. The solution was then well stirred for 30 min. at room temperature. Subsequently, the water was evaporated at a slow rate (for 3-4 h) and under stirring at 80 °C. The dried powders were then ground in a glass mortar and annealed in an 8 % H₂ in Ar (Linde, high purity) atmosphere in a Lindberg Blue HTF55000 Series hinged tube furnace (Barnstead International). A 2.5 cm diameter quartz glass tube of 85 cm length was used and the 8 % H₂/Ar gas mixture (BOC gas) was flown at a rate of 60 mL min⁻¹ over the sample during the entire heating and cooling period. The samples were heated to 100 °C starting from room temperature, and then heated at a rate of 10 °C min⁻¹ to the annealing temperature (T_a) of interest. The samples were maintained at T_a for 3 h unless otherwise stated, and then cooled at the natural cooling rate of the furnace maintaining the flow

of the H_2 in Argon gas mixture. The powders prepared in this manner are referred to as asprepared catalysts. Small amounts were annealed in this manner (< 150 mg) in order to ensure that all of the powder was exposed to the H_2 atmosphere in a uniform manner.

Thermal gravimetric analyses (TGA) experiments were also carried out to confirm that the carbon support was not lost during the heat treatment. This confirmed that the nominal metal loading and the metal loading of the as-prepared catalyst powders are identical.

It is noteworthy that other impregnation methods were also tested. For example an alkaline solution of the precursor salts was made and used for deposition onto the Pt/C precursor powder. However, initial studies revealed that a larger catalyst particle size resulted and correspondingly lower electrochemical surface areas per gram of catalyst were measured.

Pt/C catalysts: A total of three Pt/C powders were used as references for orr activity and electrochemical stability measurements. The as-prepared Pt/C precursor powder was used as reference. Furthermore, a fraction of the Pt/C precursor powder was annealed at 800 °C for 3 h under the flow of the 8 % H₂ in Argon gas mixture and also used as reference sample. The third reference powder, was a commercial Pt/C catalyst from Tanaka (Japan), namely a 46.9 wt.% Pt/C catalyst. Tanaka is considered to currently make state of the art PEMFC catalysts. Additionally, Pt/C precursor powder was annealed at 600, 400 and 250 °C in order to carry out a XRD diffraction pattern comparison to the Pt_{5.75}Fe_{5.75}Cu/C series catalysts, as discussed in the Result and Discussion section.

2.2 Electrochemical measurements

Electrodes and Cells: The majority of the electrochemical experiments were carried out using thin catalyst layers formed onto rotating disc electrodes (RDEs), as described following. Catalyst inks of 1-2 mg Pt per ml were formed by sonicating the as-prepared catalyst powders in 95 vol.% ethanol (Anachemia) for 1 h. After sonication, appropriate volumes of the inks were pipetted onto glassy carbon (GC) RDEs (Pine research). The RDEs had GC discs of 5 mm diameter and 0.2 cm² geometrical surface areas. Different amounts of the catalyst inks were pipetted onto the RDEs to achieve theoretical Pt loadings between 11 and 20 μ g per cm² RDE area. After drying in air and at room temperature, the thin catalyst layers were covered with small amounts of Nafion by applying 20 μ l of a 0.025 wt.% Nafion solution. (The latter was

made by diluting 50 μ l of a 5 wt.% Nafion solution (Aldrich) in a 10 ml mixture of water and iso-propanol of 75 to 25% volume ratios.) Again, the RDE was allowed to dry in air and at room temperature. The procedure described above essentially follows the protocol introduced by Mayerhofer et al. [27]. Thin catalyst and Nafion layer electrodes were formed in this manner, which are essential for electro-catalytic orr measurements [27,28].

All electrochemical measurements were carried out in standard two-compartment electrochemical glass cells, where the working and counter electrodes are separated from the reference electrode using a Luggin capillary. Aqueous 0.1 M HClO₄ solutions were used as electrolytes. High surface area Pt nets served as counter electrodes in all electrochemical experiments. A Hg/Hg₂SO₄ (MSE) using 1 M Na₂SO₄ as electrolyte served as reference electrode. It is noteworthy, that the MSE was used for both the orr and catalyst electrochemical stability experiments to avoid detrimental effects of chloride contamination. All potentials are referenced vs. the reversible hydrogen electrode (RHE). Preliminary experiments confirmed that the same orr activity is measured using an RHE or an MSE as reference electrode. All working electrodes were subjected to the same cleaning procedure that consisted of potential cycling at 50 mV s⁻¹ between 0.06 and 1.3 V for 70 complete oxidation and reduction cycles. These potential cycling limits were selected according to recommendations from industry and further discussed in a parallel study [29].

 O_2 reduction measurements and CO_{ads} stripping CO was adsorbed (CO_{ads}) onto the electrochemically pretreated catalysts at 0.1 V for 10 min. by bubbling CO gas through the electrolyte solution. The solution CO was subsequently removed by Ar gas bubbling for 20 min., while the potential of the working electrode was maintained at 0.1 V. Subsequently, two oxidation/reduction cycles were completed between 0.06 and 1.3 V at 10 mV s⁻¹, starting with a positive sweep at 0.1 V. The orr activities were obtained using RDE measurements carried out in, with O_2 gas saturated, 0.1 M HClO₄ electrolyte solutions. The positive sweep direction, of the cycles recorded at 10 mV s⁻¹ between 0.06 to 1.3 V, was used to measure the orr activity. The results are generally reported for a rotation rate of 1600 rpm, although, orr curves at specific rates between 400 to 2500 rpm were also recorded. All electrochemical measurements were carried out at room temperature. Electrochemical surface area and catalytic activity results are given as average values obtained from at least 4 to 6 individual electrode measurements.

2.3 Characterization of the catalysts

As-prepared catalysts are used for the physical characterizations described in the following two sections.

2.3.1 Transmission electron microscopy (TEM)

TEM samples were prepared by sonicating the as-prepared catalyst powders in ethanol. One drop of the ink was then placed onto a 300 mesh carbon-coated TEM copper grid (Marivac, Limited) and dried in air. The sample was then examined using a Philips CM20 TEM equipped with a Gatan UltraScan 1000 CCD camera and an energy dispersive X-ray spectrometer (EDS) INCA Energy TEM 200. The TEM was operated at an accelerating voltage of 200 kV using a conventional electron source, a LaB₆ filament. Bright field (BF) TEM images were taken for particle size measurements.

2.3.2 X-ray diffraction (XRD)

A Bruker D8 Advance diffractometer with Brag-Brentano geometry and using either a CuK α or a CoK α source was used to record diffractograms. A step size of 0.02 or 0.035° was used, accumulating data for 3 s at each step. The X-ray patterns are generally shown as intensity (arbritary units) vs. d-spacing in order to compare patterns collected using the two sources. The d-spacing was calculated as follows: d-spacing = $\lambda/(2\sin\theta)$. Two different X-ray sources, CuK α and CoK α , were used during the process of this work. Cross-checks were made comparing the diffraction patterns of catalysts obtained using the two different sources. Essentially the same patterns were obtained when plotted as intensity vs. d-spacing. The exception was the additional presence of a small diffraction peak at d-spacing values of 2.43 Å in the patterns acquired using the CoK α source. This diffraction peak is an artifact caused by an escape peak from CoK α radiation.

Data analysis was carried out using TOPAS version 4.2 implementing the fundamental parameters approach (FPA) [30]. The FPA line-broadening function for linear PSD implemented in TOPAS 4.2 was used to model the instrumental lineshape in the Rietveld refinement. The specimen-dependant parameters refined in the Rietveld analysis included the zero error, a user-specified number of coefficients of a Chebyshev polynomial fitting the background, and the lattice parameters of each phase. In the Rietveld refinement of each sample, an anisotropic line-

broadening was also needed for each individual phase present in order to fit the diffraction intensities adequately. The spherical-harmonics 6th-order anisotropic line-broadening function implemented in TOPAS 4.2 was used for this purpose.

2.4 Chemicals and solutions

All chemicals used were A.C.S. grade and the solutions were made using high resistivity water (18 M Ω ·cm⁻²). The electrolyte solutions were deoxygenated by bubbling high purity Ar gas for 40 min. prior to recording CVs.

3. **Results and discussion**

3.1 XRD characterization of as-prepared Pt/C, Pt₃Fe/C and PtFe/C catalysts

Fig. 1a shows the XRD patterns of the as-prepared Pt₃Fe/C and PtFe/C catalysts annealed at 600 and 800 °C. XRD patterns for the precursor Pt/C catalysts and the precursor Pt/C catalyst annealed at 800 °C are also shown for comparison in Fig. 1a. Fig. 1b shows the reference XRD stick patterns for cubic Pt (No. 87-0646), ordered cubic Pt₃Fe (No. 89-2050), ordered tetragonal PtFe (No. 65-1051), cubic Fe (No. 89-4186), and cubic Cu (No. 85-1326) from Joint Committee on Powder Diffraction Standards (JCPDS) cards. The stick patterns for disordered cubic Pt-Fe is not shown. The latter is essentially the same as for cubic Pt, except that the positions are shifted to lower d-spacing values depending on the amount of Fe dissolved in the Pt lattice. Table 2 summarizes the characteristics of the various as-prepared catalysts extracted from the corresponding XRD patterns. It is noteworthy that the nominal M to Pt atomic ratio of all these catalysts does not exceed 1:1. The following abbreviations are used to indicate the different structure types of the catalyst phases that were formed: Face centered cubic [Fm-3m] Pt, tetragonal [P4/mmm] PtFe, and face-centered cubic [Pm-3m] Pt₃Fe. Reference to body centered cubic [Im-3m] Fe is also made, which is found to be present for the as-prepared PtFe/C catalysts. However, a separate Fe phase is not present for the two Pt₃Fe/C catalysts. XRD patterns for these nominal catalyst compositions annealed for 3 h rather than 2 h were also recorded. The diffraction patterns were essentially the same indicating that an annealing time of 2-3 h is sufficient to reach the "final" state for these catalyst formulations. The broad reflection observed at 3.57 Å (Fig. 1a) arises from the carbon (Vulcan XC-72R) support. The highest intensity peak, located between 2.26 and 2.18 Å, is due to Pt (111). This diffraction peak is seen to be shifted to

lower d-spacing values for the Pt₃Fe/C and PtFe/C catalysts than compared to the Pt/C catalysts. The shift is clearly recognizable in Fig. 1a and most pronounced for the highest nominal Fe content catalyst, namely PtFe/C catalysts. This is indicative of a lattice contraction arising from the substitution of smaller Fe atoms (atomic radius of Fe: 126 pm) for larger Pt atoms (atomic radius of Pt: 139 pm). According to the phase diagram, for a Pt to Fe atomic ratio larger than 2 to 3, the bulk Pt-Fe system exhibits two ordered intermediate phases of Pt₃Fe and PtFe type structures and a disordered Pt_xFe_y solid solution with a Pt [Fm-3m] structure [21]. The crystal structures of the two ordered phases (Pt₃Fe and PtFe types) as well as the disordered Pt_xFe_y phase are shown in Fig. 2. Pt₃Fe has a cubic [Pm-3m] structure. The Fe atoms occupy the eight corner positions and Pt atoms occupy six face centered positions in the cube. PtFe is an ordered tetragonal alloy [P4/mmm], within which the Pt and Fe atoms lie on alternate lattice planes. Pt_xFe_y has a cubic [Fm-3m] structure, in which the Pt and Fe atoms are randomly distributed. The presence of superlattice reflections, such as the (110) reflections, indicate some ordering in the phases formed. The (110) superlattice reflections are located (Figs.1a and b) at d-spacing values of 2.738 and 2.722 Å for [Pm-3m] Pt₃Fe and [P4/mmm] PtFe alloys, respectively. A major difference between the different diffraction patterns are two shoulders at 1.85 and 1.33 Å (indicated by arrows in Fig. 1a) for the PtFe/C catalysts. These shoulders are due to the (002) and (202) reflections typical for a [P4/mmm] PtFe structure type. Table 2 shows the summary of the Rietveld analyses for Pt/C and Pt_xFe/C series catalysts. The Pt/C catalysts have the [Fm-3m] space group and lattice constants close to the value for bulk Pt metal. The Pt₃Fe/C catalysts have cubic structures of [Pm-3m] space group. In case of the Pt₃Fe/C(800) catalyst, the Rietveld analyses suggests that a fully ordered cubic alloy is formed, while the Pt₃Fe/C(600) catalyst shows a slight degree of disorder (two [Pm-3m] phases are used for the fitting). The lattice constants (a) values of the two alloyed catalysts are seen to be smaller than observed for the Pt/C catalysts. The PtFe/C catalysts form tetragonal alloys of [P4/mmm] space group. Both of the PtFe/C catalysts show a small percentage (1-3%) of separate Fe [Im-3m] phase. According to the Rietveld analyses, neither of the two PtFe/C catalysts forms a fully ordered alloy. This is shown in Figs. 3a and b on the example of the fit for the PtFe/C(800) catalyst. Fig. 3a shows the fit carried out using 100% of one [P4/mmm] phase. The red curve on top of the graph shows the residual, i.e., the difference between the measured diffraction intensities (blue curve) and fitted model (red curve), while the green curve shows the [P4/mmm] phase fitted. It is seen that there

is a mis-match particularly at 20 angles of 36 and 41°. The use of a slight degree of disorder in the [P4/mmm] phase, as shown in Fig. 3b, allows for a better fit and a smaller residual. As expected, the lattice constants of the [P4/mmm] phases are small and in good agreement with their Joint Committee on Powder Diffraction Standards (JCPDS) cards. The average crystallite size (d_c) for the various catalysts are also listed in Table 2. These values are calculated using the Scherrer equation and the (111) as well as (220) diffraction peaks. Individual particle size and particle size distribution results extracted from TEM images are discussed in a later section. Table 2 suggests that the d_c value for the Pt₃Fe/C and PtFe/C catalysts annealed at 600 °C is between 4 and 5 nm, while the Pt₃Fe/C and PtFe/C catalysts annealed at 800 °C have d_c values of 6 nm. The latter values are very similar to the d_c value of 5.8 nm for the Pt/C(800) catalyst, suggesting that the addition of Fe does not influence the average crystallite size of the asprepared catalysts.

In summary, it is confirmed that the utilization of a higher T_a allows for the preparation of more ordered structures of the Pt₃Fe/C and PtFe/C catalysts. In case of Pt₃Fe/C(800), a fully ordered cubic alloy is formed, while neither of the two PtFe/C catalysts form a fully ordered tetragonal alloy. Also, a small percentage (< 3%) of a separate [Im-3m] Fe phase is detected for both the PtFe/C catalysts. As expected the lattice constants decrease with increasing Fe content, i.e., Pt/C > Pt₃Fe/C > PtFe/C, which is expected to result in differences in the orr activities.

3.2 XRD characterization of as-synthesized $Pt_{5.75}Fe_{5.75}Cu/C$ catalysts formed as a function of T_a

In this section the addition of Cu to the Pt and Fe based catalyst is investigated in order to identify whether tetragonal PtFe type alloys can be formed at lower T_as . This concept has been reported for the purpose of the preparation of magnetic recording devices [22,23]. The latter studies were carried out for thin films. The same concept is explored in this work for the preparation of nano-sized electro-catalysts supported on carbon. In previous work, films of Pt:Fe atomic composition of 1:1 were made and the amount of Cu was varied. The films were then annealed at different temperatures and it was found that the Pt_{5.75}Fe_{5.75}Cu composition showed the presence of some ordering in the alloy structure already at T_a 's of 300 °C. Therefore, a set of catalysts was prepared in this work using the nominal Pt_{5.75}Fe_{5.75}Cu/C composition and different T_as . Fig. 4 shows the XRD patterns for these catalysts. The superlattice reflections at 3.7 and

2.721 Å (d-spacing values) are recognizable for T_a's of 400 and 500 °C, thus indicating the presence of ordering in the phases formed. They are clearly recognizable for the Pt_{5.75}Fe_{5.75}Cu/C catalysts annealed at 600 °C and higher T_as. The results from the Rietveld analyses are summarized in Table 3. The Pt_{5.75}Fe_{5.75}Cu/C(800) catalyst is suggested to have a single-phase [P4/mmm] tetragonal structure. Fig. 5a shows the quality of the Rietveld fit for this catalyst. A high quality fit is seen to be obtained using 100% of one [P4/mmm] phase. Unlike the PtFe/C series catalysts, the Rietveld fits do not suggest the presence of an impurity Fe [Im-3m] phase. Fig. 5b shows the details of the crystal-structure model used for the fitting. The best fit was achieved using this structure. Cu is present in every plane, while the Pt and Fe atoms are present in alternate planes, i.e., Pt and Cu are present in lattice planes corresponding to the (1/2, 1/2, 1/2)crystallographic site, while Fe and Cu occur in planes associated with the (0,0,0) site. Table 3 shows that the lattice constants of the Pt_{5.75}Fe_{5.75}Cu/C [P4/mmm] alloys are slightly smaller than those found for the PtFe/C catalysts. The average crystallite (d_c) extracted from the Pt (111) and Pt (220) peaks are also listed in Table 3. The d_c values are seen to increase with increasing T_a as expected. They are somewhat larger for the Pt_{5.75}Fe_{5.75}Cu/C vs. the PtFe/C catalysts prepared at the same T_a. It is noteworthy that the synthesis of the two catalyst series was carried out more than once from the very beginning, and the Pt_{5.75}Fe_{5.75}Cu/C series consistently showed a slightly larger average crystallite size. Therefore, the results could suggest that slightly higher kinetics of crystal growth are induced by adding Cu to form the ternary Pt_{5.75}Fe_{5.75}Cu system.

It should be noted that all the XRD patterns of the $Pt_{5.75}Fe_{5.75}Cu/C$ catalyst series could be fitted using one or two [P4/mmm] phases. However, the presence of a small amount of a single fcc Pt phase cannot be excluded with certainty for the catalyst powders annealed at lower T_a 's < 600 °C.

In summary the Rietveld analyses of the XRD patterns suggest differences in the structure of the as-prepared $Pt_{5.75}Fe_{5.75}Cu/C$ and vs. PtFe/C catalysts. The results suggest that a single-phase tetragonal [P4/mmm] structure is made utilizing a T_a of 800 °C and the $Pt_{5.75}Fe_{5.75}Cu/C$ stoichiometry. A separate [Im-3m] Fe phase is not detected for the $Pt_{5.75}Fe_{5.75}Cu/C$ series. Furthermore, the average d_c value is slightly larger for a $Pt_{5.75}Fe_{5.75}Cu/C$ vs. a PtFe/C catalyst made at the same T_a because of higher crystal-growth kinetics in the $Pt_{5.75}Fe_{5.75}Cu$ system, as suggested above.

3.3 XRD characterization of Pt_{5.75}Fe_{6.75}/C, Pt_{5.75}Fe_{5.75}Cu₂/C and Pt_{5.75}Cu_{6.75}/C catalysts

Three additional catalyst compositions were also made and studied in order to investigate whether the combination of Fe + Cu rather than M (either Fe and/or Cu) the effect of Cu onto the Pt based catalysts. Therefore, Pt_{5.75}Fe_{6.75}/C, Pt_{5.75}Fe_{5.75}Cu₂/C and Pt_{5.75}Cu_{6.75}/C catalysts were made using a T_a of 600 °C. These ratios were chosen as the Pt_{5.75}Fe_{5.75}Cu₂/C stoichiometry presents an increase in the Cu content without changing the Pt to Fe ratio. The Pt_{5.75}Fe_{6.75}/C and Pt_{5.75}Cu_{6.75}/C stoichiometry represents the same Pt to M (M=Cu+Fe) at. ratio as Pt_{5.75}Fe_{5.75}Cu/C. Fig. 6 shows the XRD pattern of the two catalysts as well as the pattern for $Pt_{5.75}Fe_{5.75}Cu/C(600)$ for comparison. The diffraction patterns for the Pt_{5.75}Fe_{5.75}Cu₂/C and Pt_{5.75}Cu_{6.75}/C catalysts are very similar. This suggests that the increase in the nominal Cu content tested here does not measurably alter the catalyst structure. It is seen that the $Pt_{5.75}Cu_{6.75}/C$ catalyst shows no superlattice structures that indicate the formation of an ordered alloy. The Pt (111) maximum position is shifted to lower d-spacing values of 2.19 Å indicating alloy formation. The d-spacing values suggest a lattice constant (a) for a cubic alloy [Fm-3m] space group of 3.821 Å. Three narrow diffraction peaks at d-spacing values of 2.09 and 1.81 Å are also observed in the pattern of the Pt_{5.75}Cu_{6.75}/C catalysts that indicate the presence of a separate cubic [Fm-3m] Cu phase. The presence of a separate Cu phase is not a surprise given the fact that the nominal Cu content is larger than the Pt content. Furthermore, these results are essentially the same as reported by Koh et al., who also reported the presence of a separate Cu phase for Pt_xCu_y/C catalysts even when annealing at 800 °C and for several hours [31]. The utilization of several hours of annealing time, as used by Koh et al., did not measurably alter the XRD pattern.

The XRD pattern for the Pt $_{5.75}$ Fe $_{6.75}$ /C(600) catalyst was essentially the same as for the PtFe/(600) catalyst powder, however, clearly showing the presence of a separate [Im-3m] Fe phase.

3.4 TEM characterization

Fig. 7 shows some examples of TEM images and corresponding histograms of selected catalysts. Images for as-prepared Pt/C, Pt/C(800), Pt_{5.75}Fe_{5.75}Cu/C(800), Pt_{5.75}Fe_{5.75}Cu/C(600) and Pt_{5.75}Cu_{6.75}/C(600) catalysts are shown in Fig. 7, and used for discussion in this work. The average size and size distribution of the Pt/C catalysts (Fig. 7a) is small, namely 2.1 ± 1 nm. As expected annealing this catalyst at 800 °C results in an increase in the size and size distribution

of the catalyst particles (Fig. 7b). The majority of the particles are between 3 and 6 nm, particles as large as 23 nm are also observed. The particle size range is ~2.5 to 24 nm for the $Pt_{5.75}Fe_{5.75}Cu/C(800)$ catalyst (Fig. 7c), i.e., similar than for the Pt/C(800) catalyst. However, the percentage of larger particles is higher for the $Pt_{5.75}Fe_{5.75}Cu/C(800)$ vs. the Pt/C(800) catalyst. This appears consistent with the average crystallite size values extracted from the corresponding XRD patterns of the $Pt_{5.75}Fe_{5.75}Cu/C(800)$ and Pt/C(800) catalysts. Fig. 7d shows the TEM image for the $Pt_{5.75}Fe_{5.75}Cu/C(600)$ catalyst. For the $Pt_{5.75}Fe_{5.75}Cu/C(800)$ catalyst ca. 20% of the particles are larger than 10 nm, while for the $Pt_{5.75}Fe_{5.75}Cu/C(600)$ catalyst most of the particles are less than 10 nm. These results suggest that larger catalyst particles are formed at higher T_a values. Fig. 7e shows the TEM image and histogram for the $Pt_{5.75}Cu_{6.75}/C(600)$ catalyst. The size and size distribution is similar to the $Pt_{5.75}Fe_{5.75}Cu/C(600)$ catalyst (Fig. 7d). Spot EDS analyses indicate the presence of Pt and Fe in individual particles. The presence of Cu in a particle cannot be confirmed, as a Cu signal resulting from the grid is present in all measurements.

3.5 Electrochemical characterization of the catalysts

3.5.1 Cyclic voltammetry (CV) and electrochemical surface area (ECSA) estimation

The as-prepared catalysts were formed into electrodes and subjected to CV experiments, as described in the experimental section. Figs. 8a to c shows examples of CVs for three catalysts: The precursor Pt/C, Pt/C(800) and the $Pt_{5.75}Fe_{5.75}/C(800)$ catalyst as a function of potential cycling. The same CV studies were carried out for all catalysts prepared and studied in this work. It was found that the CV characteristics showed essentially the same changes over a period of 50-70 potential cycles. The 70 potential cycles serve to clean and condition the catalyst electrodes prior to obtaining orr measurements, as further discussed below.

For all catalysts, the charge resulting from the adsorption and desorption reaction of molecular H ($Q_{Hads/des}$) on Pt [between ca. 0 and 0.3 V] is observed to increase as the catalyst electrodes are continuously cleaned and conditioned by potential cycling. This indicates an increase in the electro-active Pt area (ECSA) to a large extend resulting from the cleaning of the catalyst surface. This is consistent with the large oxidation current observed at potentials more positive than 0.85 V. Such initial oxidation currents are typically observed for Pt electrodes and reflect processes like the oxidation of organics adsorbed on the catalyst surface. In case of the Fe

and Cu containing catalysts small oxidation peaks in the 0.65 and 0.75 V potential range are also observed during the first cycles. This peak is seen to gradually decrease with increasing cycle number, and is not recognizable after ca. 50 cycles for all the alloy catalysts studied in this work. It is possible that this pre-peak observed in the Fe and Cu containing catalysts reflects the loss of Fe and Cu. In summary, the general behavior with potential cycling appears to be the same for all catalysts. An increase in the ESCA values with cycling is observed. The Q_{Hads/des} values can be used to estimate the ECSA values. In this work a Q_{Hads/des} to ECSA conversion factor of 210 μC per cm^2 is used. It is not known whether the presence of Fe and Cu influences the $Q_{Hads/des}$ value. However, this conversion factor is frequently used for this type of catalysts studied in e.g., 0.1 M HClO₄ [20]. The weight of Pt on the corresponding RDEs was calculated using the volume of catalyst ink pipetted onto the RDE and assuming that the amount of Pt per ml ethanol The ECSA values obtained in this manner are equals the Pt concentration in the ink. summarized in Table 4 and are shown graphically in Fig. 9a. Obviously, these numbers are somewhat mis-leading as indeed catalyst may be lost during the initial 70 potential cycles. It is seen that the ECSA values for the Pt-alloy/C(600) and Pt-alloy/C(800) catalysts are in the range of 44 to 53 m² g_{Pt}^{-1} and 41 to 43 m² g_{Pt}^{-1} , respectively. The precursor Pt/C and TKK catalysts were found to exhibit the largest ECSA values of 59 and 66 m² g_{Pt}^{-1} , respectively. These catalysts are not subjected to higher T treatments, thus likely explaining the higher ESCA values. For all the catalysts of the same nominal stoichiometry, a decrease in the ECSA value of ca. 15-25% is observed with increasing T_a from 600 to 800 °C. The influence of T_a on the ECSA value is also observed in the Pt_{5.75}Fe_{5.75}Cu/C series that shows the values for three catalysts annealed at 400, 600 and 800 $^{\circ}$ C. This trend of the ECSA with T_a for a particular nominal catalyst stoichiometry is generally consistent with the d_c values extracted from the corresponding XRD patterns (Tables 2 and 3). In case of different catalysts annealed at the same T_a, the differences in the ECSA value are within 15-20%. They do not show a clear trend with the d_c values from XRD data and particle size and size distribution measurements from TEM; for example the ECSA value of the PtFe/C(800) and Pt_{5.75}Fe_{5.75}Cu/C(800) are very similar.

It is interesting to note that the ECSA values for the Pt/C precursor catalysts are only slightly smaller than values reported by P. Strasser's research group for their 30 wt.% Pt/C commercial precursor catalyst [32]. However, the ECSA values for the alloy catalysts studied in this work are significantly lower than the values reported by the latter group [31,32]. The latter

group reports high orr mass activities for some alloy catalysts that are electrochemically dealloyed. Their de-alloying procedure consists of potential cycling, although, often in a MEA and sometimes utilizing somewhat different potential limits, namely 0.5 and 1 V vs. RHE, than used in this work. They achieve higher ECSA values for some of their electrochemically de-alloyed catalysts than for their precursor Pt/C catalysts [32]. This trend is opposite the trend observed in this work and may or may not be related to differences in the potential cycling (de-alloying) procedure and/or differences in the type of alloys and Pt to ad-metal ratios. An increase in the ECSA values for all catalysts is observed in this work as a result of the potential cycling procedure. However, the increase never exceeds more than 30%, and the ECSA values of the alloy catalysts are always lower than the values estimated for the Pt/C precursor catalyst.

It is also noteworthy that ECSA values were also estimated from CO_{ads} stripping voltamograms in this work. The shape of the CO_{ads} stripping CVs of the various catalysts is not analyzed, as it is well-known that the shape of the CO_{ads} stripping voltamogram is influenced by many factors such as catalyst particle size, alloy content, sweep rate, etc. The main purpose of the CO_{ads} stripping voltamograms is to obtain another estimate of the electrochemical Pt surface area and compare the values to the numbers extracted from the H_{ads/des} peaks. A CO_{ads} stripping charge to surface area conversion factor of 420 μ C cm⁻² was used. Similar results (within 10%) were found using either the H_{ads/des} or the CO_{ads} stripping charge method.

In summary, the behavior of all these catalysts with potential cycling is similar, as an increase in the ECSA value is observed to take place during the first 50 cycles. It is likely that the increase is related to the cleaning of the electrode surface from adsorbed organics. In case of the Fe and Cu containing catalysts the ECSA value is somewhat larger than observed for an "equivalent" [same T_a] Pt/C catalyst. This may be due to an increase in surface area due to Fe and/or Cu leaching. The CV characteristics for the Fe and Cu containing catalysts all show evidence for Fe and Cu leaching during the first (< 50) CV cycles.

3.5.3 The orr reaction

The catalysts prepared in this work were evaluated for their activity for the electrochemical reduction of O_2 (orr). This was done using RDE experiments and thin layer electrode set-ups described in the literature [27] and the experimental section. In this work, the mass and specific orr activities are typically reported at 1600 rpm and for room temperature (20)

 \pm 2 °C). As discussed above, for all catalysts tested, the cycling procedure cleans the catalyst surface and essentially the same CVs are obtained within 70 cycles for a particular electrode. Experiments were also carried out at different rpm's to ensure that the electrodes obey the well-known Koutechy-Levich equation. It was confirmed that a 4 e⁻ reaction takes place for these catalysts.

Examples of orr data for the positive sweep recorded 10 mV s⁻¹ and at 1600 rpm are shown in Figs. 10a and b. Fig. 1a shows the data for the Pt/C precursor catalysts, Pt/C(800), Pt₃Fe/C(800), PtFe/C(800) and Pt_{5.75}Fe_{5.75}Cu/C(800) catalysts, while Fig. 10b shows the reproducibility for different electrodes made using the Pt_{5.75}Fe_{5.75}Cu/C(800) catalyst. The j_{lim} values for all catalysts are similar. They are also close to the theoretical value of 6 mA cm⁻² for 1600 rpm at 20 °C. Slight deviation in j_{lim} for these type of electrodes are common [27]. It is noteworthy that orr measurements were obtained for different catalyst loadings on the RDE using the protocol described by Mayrhofer et al. [27]. It was confirmed that the catalyst loadings utilized in this work fall within a range that yields mass and specific orr activities independent of the amount of catalyst on the RDE. As discussed by Mayrhofer et al. [27], the optimal catalyst loading range depends on the actual catalyst.

Table 4 summarizes the values for mass and specific orr activities for the various catalysts measured at 0.9 V. Relative error values are also given for each catalyst. These values are calculated for different electrodes made using the same catalyst. It is seen that the relative error in the orr measurements is different depending on the catalyst; it is generally between 5 and 15%. Relative errors of less than 10% appear small for orr measurements. It is likely that the actual error is easily 15%. The orr measurements are taken in a range where the current changes in an exponential manner with the potential. Therefore, even a small change in the potential of the reference electrode can affect the estimated orr activities. Furthermore, making electrodes from inks may result in irreproducible amounts of catalyst deposited onto the RDE. Based on this, a real error of > 10% in the orr measurements appears more likely. It was observed that the electrodes made using catalysts at 600 °C tended to be of visually better quality (the catalyst being homogenously spread over the electrode surface), of lower relative error than the catalysts annealed at 800 °C. Electrodes and orr data of poor quality such as low j_{lim} values were disregarded and not included in the results shown in this work. The specific and mass activity orr data, measured at 0.9 V, are summarized in Table 4 and Figs. 9b and c, respectively. The

mass activity for the home made Pt/C catalyst is 110 mA per mg Pt at 0.9 V. This is a very acceptable value and is in fact essentially the same value as found for the "state-of-the-art" Pt/C(TKK) catalyst. The orr mass activity for the Pt/C(800) catalyst is lower, namely 73 vs. the 110 mA mg⁻¹_{Pt} for the Pt/C and Pt/C(TKK) catalysts. This is expected, as the Pt surface area (ECSA value) is also seen to be decreased as a result of annealing at 800 °C. The mass and specific orr activities for the Fe and/or Cu containing catalysts are higher than for the Pt/C catalysts. According to the results, the Pt_{5.75}Fe_{5.75}Cu/C catalysts show the highest specific activities. The results could suggest that a fully ordered [P4/mmm] catalyst structure has the highest catalytic orr activity. However, it needs to be noted that the particle size is somewhat larger for the Pt_{5.75}Fe_{5.75}Cu/C vs. the equivalent PtFe/C catalysts, which may also contribute to the catalytic orr activity. Highest mass orr activities are also achieved for the Pt_{5.75}Fe_{5.75}Cu/C catalysts is not as pronounced due to the lower surface area of the former. The results also suggest that higher catalytic and mass orr activities are achieved for the [P4/mmm], the tetragonal catalysts vs. the [Pm-3m] and [Fm-3m], cubic, catalyst series.

Overall, these results suggest that the fully ordered tetragonal alloys show the highest orr activities. An enhancement in the orr mass activity of 2.8 times was found over the state of the art Pt/C catalyst, while enhancements of 4.3 times could be achieved in terms of specific activity. Comparison of orr results with literature data needs some precaution, as minor differences in making the inks, electrodes, preconditioning, and electrode potentials can result in largely different orr values. Some of the best orr results recently reported are for electrochemically dealloyed catalysts [31,32]. In some cases, the authors report 4-5 times higher mass orr activity than compared to their Pt/C precursor catalyst. This increase is higher than found for the best alloy catalyst made in this work. However, the specific orr activities of the tetragonal alloy catalysts made in this work (ca. 700 μ A cm⁻²_{Pt}) are similar, and even higher than reported for a number of the de-alloyed catalysts [31,32]. Therefore, the observed lower mass orr activity may be related to lower ECSA values of the catalysts made in this work. Obviously, it would be of interest to explore whether a fully alloyed [P4/mmm] Pt5.75Fe5.75Cu/C catalyst of higher ECSA can be made and whether a higher mass orr activity can be achieved. The highest mass orr activity enhancement of ca. 3 times over the Pt/C catalyst found in this work is higher than reported by Xiong et al. [10] for a well ordered PtCo/C catalyst. The latter reported a ca. 2 times

enhancement, although, they obviously used a different Pt/C catalyst as baseline than used in this work. However, the ca. 3 enhancement is comparable to recent work by Schulenburg et al., who studied catalysts of nominal PtCo₃ composition [20]. The mass orr activity and ECSA values of the Pt_{5.75}Cu_{6.75}/C catalyst made in this work are 2.5 and 2.1 times, respectively lower than for the best performing de-alloyed Pt-Cu/C catalyst made by Strasser's group [31]. The conditions the latter used to make and subsequently electrochemically treat their catalysts are somewhat different than applied in this work. Nevertheless, the fact that the difference in mass orr activity and ECSA values of the Pt_xCu_y/C catalyst are similar may suggest that the higher ECSA area rather than the catalytic properties are responsible for the higher mass orr activities reported by them. Cho et al. [24] also reported orr results for Pt_xFe_yCu_z/C catalysts rather than PtFe/C was made. They characterized their catalysts using EXAFS and found that the highest orr activity (in hot H₃PO₄ electrolyte) and lowest Pt-Pt bond was achieved using the tetragonal Pt_xFe_yCu_z/C catalysts.

4. Conclusions

Various carbon supported Pt/C, and binary and ternary Pt-alloy/C catalysts were prepared. A classical wet impregnation method that consisted of impregnating a preformed Pt/C catalyst powder with Fe and/or Cu-nitrate precursor salts in slightly acidic solutions was utilized. The final Pt_xFe_y/C , $Pt_xFe_yCu_z/C$ and Pt_xCu_y/C catalysts were obtained by annealing the impregnated samples in a H₂ enriched atmosphere. X-ray diffraction (XRD) patterns and Rietveld analyses revealed that the following structures were formed: Cubic ordered [Pm-3m] for Pt₃Fe/C, tetragonal ordered [P4/mmm] for PtFe/C and Pt_{5.75}Fe_{5.75}Cu/C and cubic disordered [Fm-3m] for Pt_{5.75}Cu_{6.75}/C. (All catalyst compositions are given as nominal stoichiometries.) Rietveld analyses also suggests that the Pt₃Fe/C and Pt_{5.75}Fe_{5.75}Cu/C catalysts annealed at 800 °C consist of a single ordered cubic and a single ordered tetragonal phase, respectively. The PtFe/C catalysts were found to contain a few percent of a separate Fe phase, i.e., a single fully ordered structure was not achieved. The XRD results suggest that the combination of Cu with PtFe appears to be beneficial in achieving a fully ordered [P4/mmm] phase catalyst. It should be noted that the average crystallite sizes extracted from the XRD patterns suggests a ca. 20% larger size for the $Pt_{5.75}Fe_{5.75}Cu/C$ vs. PtFe/C analog catalysts. This appears consistent with the electrochemical Pt surface areas estimated from the CV data that revealed a slightly lower (ca. 5%) surface area for $Pt_{5.75}Fe_{5.75}Cu/C$ vs. PtFe/C analog catalysts.

The as-prepared catalysts were also characterized for their electrochemical activity towards the O₂ reduction reaction (orr) in a thin electrode set-up and compared to the precursor Pt/C catalysts, a state of the art Pt/C catalyst from Tanake and the precursor Pt/C catalyst annealed at 800 °C. The first two show the same orr mass activity, and are referred to as baseline catalysts. The specific and mass orr activities of all alloy catalysts are higher than for the Pt/C only catalysts. The specific orr activity of the Pt_{5.75}Fe_{5.75}Cu/C catalysts is higher than for the PtFe/C and the Pt₃Fe/C as well as for the Pt_{6.75}Cu_{5.75}C catalysts. Furthermore, the specific orr activities for the Pt_{5.75}Fe_{5.75}Cu/C catalysts are comparable or even higher than for highly active (mass orr) catalysts reported in the literature [31,32]. The latter are referred to as de-alloyed catalysts of 4-5 times have been reported. The mass orr activity enhancements of the alloy catalysts in this work are lower (2.8 times) than the 4-5 times reported for de-alloyed catalysts. However, both the mass and surface area values of the alloy catalysts made in this work are proportionally lower than reported for the de-alloyed catalysts. Therefore, it is concluded that in terms of catalytic activity similar orr catalysts are made.

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Catalyst	W	W		
	$[Fe(NO_3)_3 \cdot 9H_2O]$	$[Cu(NO_3)_2 \cdot 6H_2O]$		
	/ g	/ g		
Pt ₃ Fe/C	0.0691	0		
PtFe/C	0.2072	0		
Pt _{5.75} Fe _{6.75} /C	0.243	0		
Pt _{5.75} Fe _{5.75} Cu/C	0.2072	0.0266		
D t E C (C	0 2072	0.0521		
Pt _{5.75} Fe _{5.75} Cu ₂ /C	0.2072	0.0531		
$\mathbf{P}_{\mathbf{f}} = -\mathbf{C}_{\mathbf{H}} = -\mathbf{c}_{\mathbf{C}}$	0	0.0623		
r 15.75Cu _{6.75} /C	0	0.0025		

Table 1 Weights of precursor salt impregnated onto 0.5 g of 20 wt.% Pt/C precursorcatalyst

Sample	$d_c^{\#}$	phase	weight	а	С	Site* occ.	Site occ.
	/	type	/ %	/ Å	/ Å	0,0,0	1/2,1/2,1/2
	nm					or	
						1⁄2,0,0	
Pt/C	2.1	Fm-3m	100	3.9273(1)	n.a.	Pt=1	n.a.
Pt/C	5.8	Fm-3m	100	3.92443(8)	n.a.	Pt=1	n.a.
(800)							
Pt ₃ Fe/C	6	Pm-3m	100	3.87221(6)	n.a.	Pt=1	Fe=1
(800)							
Pt ₃ Fe/C	4.5	Pm-3m	26(18)	3.857(2)	n.a.	Pt=1	Fe=1
(600)		Pm-3m	74(18)	3.8971(3)	n.a.	Pt=0.514,	Fe=0.542,
						Fe=0.480	Pl=0.438
PtFe/C	6.1	P4/mmm	97.4(6)	2.72488(9)	3.7312(2)	Fe=0.919,	Pt=0.924,
(800)		Im_3m	26(6)	2,806(1)	na	Pt=0.081 Fe=1	Fe=0.076
		111-5111	2.0(0)	2.090(1)	11 . a.	10-1	
PtFe/C	6.1	P4/mmm	21(4)	2.7069(5)	3.709(1)	Fe=1	Pt=1
(600)		P4/mmm	77(4)	2.7434(4)	3 7734(8)	Fe=0.451	$P_{t=0}$ 540
		1 4/11111111	//(+/	2.7734(4)	5.7754(0)	Pt=0.431, Pt=0.549	Fe=0.349, Fe=0.451
		Im-3m	1.6(3)	2.9014(6)	n.a.	Fe=1	

Table 2 Structure for Pt series catalysts extracted from XRD pattern

#: Average crystallite size (d_c) calculated from Pt(111) or Pt(220) peaks using Scherrer's equation.

*: Atom site 0,0,0 corresponds to Pt [Fm-3m], PtFe [P4/mmm], and Fe [Im-3m] structure types; while atom site $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ refers to PtFe [P4/mmm] and Pt₃Fe [Pm-3m] structure types.

Ta	$d_c^{\#}$	Phase	weight	a /Å	c / Å	Site	Site
/	/nm		/ %			occ.	occ.
°C						0,0,0	1/2,1/2,1/2
800	7.5	P4/mmm	100	2.7332(1)	3.7121(3)	Fe=0.92,	Pt=0.92,
						Cu=0.08	Cu=0.08
650	6.9	P4/mmm	40	2.7196(2)	3.7140(5)	Fe=0.92,	Pt=0.92,
						Cu=0.08	Cu=0.08
		P4/mmm	60	2.7344(7)	3.755(2)	Fe=0.80,	Pt=0.7,
						Pt=0.12,	Fe=0.2,
						Cu=0.08	Cu=0.08
600	4.9	P4/mmm	49	2.753(1)	3.792(2)	Fe=0.92,	Pt=0.92,
						Cu=0.08	Cu=0.08
		P4/mmm	51	2.7123(2)	3.7236(7)	Fe=0.92,	Pt=0.59,
						Cu=0.08	Fe=0.33,
							Cu=0.08
500	4.7	P4/mmm	100	2.7400(5)	3.819(2)	Fe=0.35,	Pt=0.35,
						Pt=0.57,	Fe=0.57,
						Cu=0.08	Cu=0.08
400	4.4	P4/mmm	27	2.725(2)	3.735(3)	Fe=0.92,	Pt=0.92,
						Cu=0.08	Cu=0.08
		P4/mmm	73	2.7406(5)	3.807(1)	Fe=0.44,	Pt=0.48,
						Pt=0.48,	Fe=0.44,
						Cu=0.08	Cu=0.08
300	3.5	P4/mmm	6.3	2.747(6)	3.70(1)	Fe=0.92,	Pt=0.92,
						Cu=0.08	Cu=0.08
		P4/mmm	93.7	2.7603(5)	3.813(1)	Fe=0.41,	Pt=0.51,
						Pt=0.51,	Fe=0.41,
						Cu=0.08	Cu=0.08
250	3.3	P4/mmm	3.6	2.735(9)	3.73(2)	Fe=0.92,	Pt=0.92,
						Cu=0.08	Cu=0.08
		P4/mmm	96.4	2.7706(5)	3.820(1)	Fe=0.42,	Pt=0.50,
						Pt=0.50,	Fe=0.42,
						Cu=0.08	Cu=0.08

Table 3 Structure for Pt_{5.75}Fe_{5.75}Cu/C series catalysts

#: Average crystallite size (d_c) calculated from Pt(111) or Pt(220) peaks using Scherrer's equation.

Sample	ECSA	j 0.9 v	j _{lim}	Mass	Specific
	$/ m^2 g_{Pt}^{-1}$	/ mA cm ⁻²	$/ \mathrm{mA \ cm^{-2}}$	Activity	Activity
				(0.9 V)/	(0.9 V)/
				$mA mg_{Pt}^{-1}$	$\mu A \text{ cm}^{-2}_{Pt}$
Pt/C(TKK)	66±2%	1.2±2%	5.4±7%	112±2%	170±2%
Pt/C	59±8%	1.2±8%	5.7±2%	109±9%	185±9%
Pt/C(800)	34±18%	0.74±14%	5±4%	73±14%	215±13%
Pt ₃ Fe/C(800)	42±14%	1.7±2%	5.4±2%	216±2%	514±2%
PtFe/C(800)	39±5%	1.9±4%	5.45±2%	230±4%	589±4%
Pt _{5.75} Fe _{5.75} Cu/C(800)	38±13%	2.1±7%	5.2±4%	283±14%	744±3%
Pt ₃ Fe/C(600)	52±8%	1.7±4%	5.8±3%	201±3%	386±4%
PtFe/C(600)	47±13%	2±5%	5.6±4%	272±8%	578±8%
Pt _{5.75} Fe _{6.75} /C(600)	47±13%	2.1±5%	5.7±4%	260±8%	553±8%
Pt _{5.75} Fe _{5.75} Cu/C(600)	44±9%	2.1±5%	5.4±6%	310±6%	704±6%
Pt _{5.75} Cu _{6.75} /C(600)	42±5%	1.6±6%	5±4%	210±10%	500±10%

Table 4 ECSA and orr activity for various carbon supported catalysts

The percentage errors shown in the Table above are relative errors obtained from the experimental data for different electrodes carried out using the same catalyst.

Figure caption

Figure 1 Fig. 1a shows XRD patterns of as-prepared Pt/C and Pt_xFe_y/C catalysts. Fig. 1b shows the XRD stick patterns of face-centered cubic Pt (JCPDS 87-0646), ordered cubic Pt_3Fe (JCPDS 89-2050), ordered tetragonal PtFe (JCPDS 65-1051), body-centered cubic Fe (JCPDS 89-418-6) and face-centered cubic Cu (JCPDS 85-1326).

Figure 2 Crystal structure of disordered Pt_xFe_y alloys [Fm-3m] and ordered tetragonal PtFe [P4/mmm] and ordered cubic Pt_3Fe [Pm-3m].

Figure 3 Example of Rietveld analyses fit for the PtFe/C(800) catalyst. Fig. 3a shows the fit using 100% of one P4/mmm phase, Fig. 3b shows the same, however, introducing a slight degree of disorder in the P4/mmm phase. In the graphs, the red shows the fitted Rieveld model, green the P4/mmm phase, black the background and blue the experimental data (diffraction intensities). The red line on top shows the discrepancy between fitted and experimental data.

Figure 4 XRD patterns of the $Pt_{5.75}Fe_{5.75}Cu/C$ series catalysts prepared at different annealing temperatures, as indicated in the figure.

Figure 5 Example of Rietveld analyses fit for the $Pt_{5.75}Fe_{5.75}Cu/C(800)$ catalyst. A fully ordered, i.e., 100% of one P4/mmm phase is used for the fit. In the graph, the red shows the fitted Rieveld model, green the P4/mmm phase, black the background and blue the experimental data (diffraction intensities). The red line on top shows the discrepancy between fitted and experimental data.

Figure 6 XRD patterns of as-prepared $Pt_{5.75}Fe_{5.75}Cu/C(600)$, $Pt_{5.75}Fe_{5.75}Cu_2/C(600)$ and $Pt_{46}Cu_{64}/C(600)$ catalysts.

Figure 7 TEM images and corresponding histograms of as-prepared catalysts, as follows: Precursor Pt/C in Fig. 7a, Pt/C(800) in Fig. 7b, $Pt_{5.75}Fe_{5.75}Cu/C(800)$ in Fig. 7c, $Pt_{5.75}Fe_{5.75}Cu/C(600)$ in Fig. 7d and $Pt_{46}Cu_{64}/C(600)$ in Fig. 7e.

Figure 8 Background CV examples recorded at 50 mV s⁻¹ as a function of the cycling number in 0.1 M HClO₄. The y-axes show the current density measured per geometrical RDE area. Fig. 8a shows the results for the precursor Pt/C, Fig. 8b for Pt/C(800), Fig. 8c for Pt_{5.75}Fe_{5.75}Cu/C(800) catalyst. The Pt loadings in μ g cm⁻² on the RDE were: 14 for Pt/C, 12 for Pt/C(800) and Pt_{5.75}Fe_{5.75}Cu/C(800).

Figure 9 ECSA (a), orr mass activities (b) and orr specific activities (c) of catalysts prepared and studied in this work. The mass and specific orr activities are measured at 0.9 V vs. RHE. The yellow, black and red columns indicate the results for catalysts annealed at 400, 600 and 800 °C, respectively. The dotted line indicates the results for the precursor Pt/C catalyst.

Figure 10 Various orr curves recorded at 1600 rpm and 10 mV s⁻¹ in 0.1 M HClO₄. Fig. 10a shows the curves for precursor Pt/C (black), $Pt_3Fe(800)/C$ (light blue), PtFe(800)/C (pink), $Pt_{5.75}Fe_{5.75}Cu/C(800)$ (dark blue). Fig. 10b shows curves for three different electrodes prepared

using $Pt_{5.75}Fe_{5.75}Cu/C(800)$. The Pt loadings in $\mu g \text{ cm}^{-2}$ on the RDE were: 14 for Pt/C, 14.5 for $Pt_3Fe/C(800)$ and PtFe/C(800) and 15 for $Pt_{5.75}Fe_{5.75}Cu/C(800)$.



Fig. 1a



Fig. 1b



Figure 2



Fig. 3a



Fig. 3b



Figure 4



Fig. 5a



Fig. 5b



Figure 6





Fig. 7a





Fig. 7b





Fig. 7c















Fig. 8a



Fig. 8b



Fig. 8c



Fig. 9a



Fig. 9b



Fig. 9c



Fig. 10a



Fig. 10b