We report on the polymeric surfactant-assisted synthesis and characterization of highly dispersed, uniformly alloyed Cu-rich Pt–Cu bimetallic nanoparticles with Cu contents up to 75 atom % Cu for use as an oxygen reduction reaction (ORR) electrocatalyst at polymer electrolyte membrane fuel cells (PEMFC) cathodes. Depending on alloy composition, catalyst format, and surface structure, the observed specific, that is, Pt surface-area normalized, activity enhancements compared to pure Pt varied from a factor of two to three times for high surface-area particles to over ten times for single-crystal alloy surfaces. The enhanced ORR activity in Pt alloys was ascribed to surface roughening, electronic structure modifications of Pt by neighboring base metal (sub)surface atoms, and modifications in the geometric structure of the electrocatalytic surface. The investigation of enhanced ORR activity of Pt alloys has been conducted on bulk alloys, on sputtered thin films, but has lately been focusing on carbon supported high-surface-area nanoparticles. The most common method to synthesize carbon-supported Pt–M alloy nanoparticles using liquid precursor methods involves the impregnation of Pt salt solutions and one or more non-Pt metal salt solutions onto high-surface-area carbon supports followed by annealing at elevated temperatures (>500°C) under hydrogen (“impregnation/reduction” method). The annealing under flowing hydrogen at elevated temperature serves a twofold purpose: first, it helps reduce the base metal salt to the metallic state, and, second, it enables the formation of a well-alloyed, homogeneous single-phase Pt–M alloy material. The preparation of uniformly alloyed Pt-rich alloys (Pt content ≥75 atom %, for instance, Pt50Cu50) can be achieved at moderate temperatures (500–700°C) at relatively short annealing times (2–7 h). Base-metal rich Pt–M alloy materials, however, that is, alloys with base metal content of ≥50 atom %, requires high temperature annealing (>700°C) for extended periods of time to obtain single-phase alloys. Base-metal-rich Pt alloy electrocatalysts have been reported to offer superior surface electrocatalytic activity after removal of surface segregated Cu by electrochemical dealloying. reported the synthesis of a carbon-supported Pt50Cu50 catalyst at 950°C, annealed for 7 h, and still observed a two-phase alloy material. High-temperature treatment for extended periods of time results in undesired increases in mean particle size and in broad particle size distributions. As a result of this, the active electrochemical surface area and, consequently, the Pt mass-based activity of the electrocatalytic nanoparticles are significantly reduced.

To mitigate the problem of surface-area loss (particle growth) during catalyst preparation, surfactant-assisted metal reduction methods have been developed. Uniformly alloyed (single-phase) Pt–M nanoparticle catalysts with relatively narrow size distribution and high surface area have been obtained. Common surfactants include, among many others, functionalized anionic, cationic, or nonionic long-chain alkyl compounds. The synthesis can be performed in a one- or two-phase (emulsion) mixture of solvent and reducing agent. The use of diols or polyols as the reducing agents in high boiling point solvent has come to be referred to as the “poly-ol process.” Since the surfactants remains bonded on the surface of the alloy nanoparticles after synthesis, site blocking results in low electrocatalytic activities and therefore requires careful removal of the surfactant prior to catalytic testing.

Functionalized polymers have also been used to prepare Pt alloy nanoparticles with small mean diameter and narrow size distribution. Polymeric surfactants offer the advantage that proper choice of polymer properties can eliminate the requirement of complete surfactant removal because electrochemical powder electrocatalysts are typically tested in a polymer/catalyst composite film format. Choi and Woo showed that PtRu nanoparticles dispersed in electronically conductive poly(N-vinyl carboxole) and poly(9-(4-vinylphenyl)carboxole) have some potential for DMFC anode catalyst applications. Colloidal Pt and Pd alloy cluster dispersions protected by nonionic polymers, such as poly(N-vinyl-2-pyrrolidone) (PVP), were prepared by reduction of the corresponding metal hydroxide in a cold alloying process. Ionomically conductive polymers (so-called polyelectrolytes), such as polystyrene sulfonic acid (PSS) (negatively charged) or poly(diallyldimethylammonium chloride) (PDDA) (positively charged) were used to prepare stabilized, narrowly dispersed Pt nanoparticles for use as unsupported fuel cell electrocatalysts. Their structural and chemical affinity to PEMFC polymer electrolytes, such as Naion, makes PSS- or PDDA-stabilized Pt particles suitable for use in PEMFC cathodes. Jiang et al. showed that the positive charges of PDDA allowed the self-assembly of (PDDA–Pt) composite films onto Naion fuel cell membrane surfaces due to the Coulomb interaction with the negatively charged sulfonic groups. The PDDA-stabilized Pt nanoparticles have shown potential electrocatalytic activity for oxygen reduction reaction in PEMFCs and methanol oxidation reaction in DMFCs. In this contribution, we report on the synthesis and electrocatalytic activity of oxygen reduction reaction in PEMFCs and methanol oxidation reaction in DMFCs.
UV-visible spectroscopy.— UV-visible spectroscopy was used to characterize the formation of platinum and its alloy nanoparticles using UV-visible spectroscopy (HP 8350) before and after reflux. The sample was diluted to 10⁻⁴ M Pt. The UV-visible spectroscopy was obtained for sample after calibration with blank solution.

X-ray diffraction (XRD).— Laboratory-source XRD was conducted to characterize the structure of the electrocatalysts using a Siemens D5000 (0/2θ) diffractometer equipped with a Braun (Garching Germany) position sensitive detector (PSD) with an angular range of 8°. The Cu Ko source was operating at a potential of 35 kV and a current of 30 mA. 2θ diffraction angles ranged from 20° to 70°, using step scans of 0.02°/step and a holding time of 10 s/step. Advanced X-ray Solution (X-ray commander, Bruker AXS) software was used to control the diffractometer from a desktop computer. Particle sizes were estimated using the Scherrer equation.

Transmission electronic microscopy (TEM).— Pt and its alloy nanoparticles were examined by TEM (JEOL 2010) under accelerating voltage of 200 kV. The TEM sample was obtained by dipping one drop of diluted colloidal solution on a copper grid coated with carbon film and allowed to dry at room temperature. Particle size and size distribution were obtained by measuring more than 100 particles from the enlarged TEM images.

Electrochemical characterization of supported nanoparticles.— The rotating disk electrode (RDE) technique was used to evaluate the electrocatalytic activity of platinum and platinum alloy nanoparticles using Gamry instruments and a Pine rotator.

To prepare carbon-supported nanoparticles, high surface-area carbon (Vulcan XC-72) was added to a dispersion consisting of the synthesized nanoparticles and isopropanol, followed by ultrasonication for ~1 h (Branson D150). By sonication, the nanoparticles were highly dispersed into the solution and brought into close contact with the porous carbon support. Possibly supported by surface charge interactions, the nanoparticles were quantitatively transferred into the carbon pores. For both pure Pt and Pt alloy particles, the carbon weight was chosen such as to obtain a final Pt loading of ~20 wt % assuming a quantitative uptake of particles onto the carbon.

Catalyst inks using unsupported and carbon-supported nanoparticles as well as the commercial catalysts were prepared by ultrasonically mixing the catalysts with appropriate amounts of water, isopropanol, and Nation solution. A 10 μL aliquot was dispersed onto a 5 mm glassy carbon (GC) working RDE. The GC-RDE was prepared with diamond and alumina paste (5, 1, and 0.05 μm, Buehler Inc.) and subsequently rinsed with water. The RDE was then precoated with a mixture of Nation and carbon powder (Vulcan XC-72). The Nation content of this mixture was ~30 wt %. The geometric platinum loading on the RDE was ~12 μg cm⁻². 0.1 M HClO₄ was prepared from suprapure concentrated HClO₄ (Aldrich) and used as electrolyte. A platinum gauze and calomel electrode were used as the counter-electrode and reference electrode, respectively. All the potentials were normalized to reversible hydrogen electrode (RHE) under the same condition. Cyclic voltammograms (CVs) were recorded in N₂-saturated electrolyte without rotation. The potential was scanned in the range of 0.05–1.0 V vs RHE at the scan rate of 100 mV/s. Linear sweep voltammograms (LSVs) were conducted in O₂-saturated electrolyte under 1600 rpm by scanning the potential in the anodic direction from 0.05 V to 1.0 V vs RHE at the scan rate of 5 mV/s. Mass and specific activities were obtained at 0.9 V vs RHE after mass-transportation correction.

Results and Discussion

PDDA-assisted polyl synthesis of Cu-rich Pt–Cu bimetallics.— The first two columns of Table I summarize the stoichiometries and synthesis conditions of PDDA-stabilized Pt–Cu alloy particles prepared and discussed in this section. The polyl method has
been used successfully in the past in order to prepare uniformly alloyed Pt-rich nanoparticles at relatively low temperatures below 200°C for a wide range of functional applications. Here, focus is placed on Cu-rich Pt–Cu bimetallics for use as ORR electrocatalysts, which are notoriously difficult to prepare as uniformly alloyed particles at temperatures as low as 200°C. An illustration of the possible structure of the resulting PDDA-stabilized Pt–Cu bimetallic nanoparticles is provided in Fig. 1b.

**UV-vis characterization.**— Figure 2 shows the UV-visible spectrum of solutions containing PDDA, H2PtCl6, their mixture, and PDDA–Pt nanoparticles. PDDA is almost transparent under UV-vis spectrum. For H2PtCl6 solution, there were two absorbance peaks at 201 nm and 269 nm, characteristic absorbance of platinum complex of PtCl42− and PtCl62−, respectively. After mixing with PDDA, the absorbance peak at 201 nm did not change, but the absorbance peak at 269 nm shifted to 269 nm with a significant increase in the absorbance. This can be ascribed to the strong coordination of the positively charged N atoms in PDDA to PtCl62− ions.

The mixture of PDDA and H2PtCl6 was pale yellow. After the reaction, the color of the solution changed to dark brown. At the same time, the absorbance peaks at 201 nm and 269 nm were no longer visible, suggesting that all Pt ions were reduced by the EG polyol.

Figure 3 shows the UV-vis spectra of solutions containing PDDA–Pt, PDDA–PtCu, and PDDA–PtCu3 colloidal solutions. Unlike PDDA–Pt, PDDA–Cu shows a characteristic absorbance peak at 568 nm due to plasma oscillations characteristic for Cu surfaces. The weakening of this absorption peak for PDDA–PtCu and PDDA–PtCu3 colloidal solutions in Fig. 3 suggests the formation of well-alloyed Pt–Cu bimetallic nanoparticles. The redshifted weak and very broad absorption bands after synthesis for the PDDA–PtCu and PDDA–PtCu3 particles further suggest a surface-segregated Cu-shell structure previously observed in similar systems.

**X-ray structural analysis.**— Figure 4 shows the XRD patterns of PDDA-stabilized nanoparticles. For H2PtCl6 solution, there were two absorbance peaks at 900°C. The diffraction peaks at 2θ of 39.8°, 46.2°, 67.4° for PDDA–Pt nanoparticles can be indexed to the 111, 111, and 200 reflections of PtCl62−, respectively. The characteristic absorbance of platinum complex of PtCl42− and PtCl62−, respectively. After mixing with PDDA, the absorbance peak at 201 nm did not change, but the absorbance peak at 269 nm shifted to 269 nm with a significant increase in the absorbance. This can be ascribed to the strong coordination of the positively charged N atoms in PDDA to PtCl62− ions.

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strongly suggests that the PDDA–PtCu and PtCu nanoparticles were neither a mere mixture of pure Pt and Cu nor contained significant amounts of unalloyed residual metals. Instead, the PDDA-stabilized PDDA–Pt–Cu nanoparticles were highly dispersed base-metal-rich nanoparticles with narrow size distributions. Further inspection of Fig. 5d showed that PtCu3 nanoparticles by impregnating the Pt/C catalyst with the Cu precursor and annealing under H2/Ar atmosphere at 900°C (row 7 in Table I). Although the authors reported single-phase particles, the resulting particle size was much larger than that of PDDA–PtCu nanoparticles. In order to directly compare particle characteristics at high Cu contents, PtCu3 nanoparticles were synthesized using impregnation/reduction at 600°C and 950°C. Figure 4b shows the XRD profiles of the annealed alloy materials. The alloy particles annealed at 600°C showed unalloyed residual Cu, and (111) peak shoulders suggest multiple alloy phases. A peak analysis (Table I) reveals the presence of two alloy phases (row 8 in Table I). Similarly, the PtCu alloy prepared at 950°C exhibited multiple alloy phases of relatively large particle size based on their small full width at half maximum (fwhm). As expected at higher annealing temperatures, no residual Cu diffraction peak was detected. Our comparative study showed that polymer-assisted polyol methods enable the synthesis of uniformly alloyed single phase Cu-rich Pt–Cu bimetallic particles at temperatures below 200°C. The resulting alloy particles are characterized by smaller mean particle size compared to the conventional impregnation/annealing methods.

**TEM analysis.**—Figure 5 shows the TEM images and size distributions of PDDA-stabilized unsupported Pt and Pt–Cu nanoparticles in comparison to carbon-supported PtCu alloy particles synthesized by a conventional impregnation/reduction method and annealed at 600°C for 7 h. Figures 5a–c are evidence that, using PDDA stabilization, the average particle size of Pt and Pt–Cu alloys can be maintained at a narrow size distribution with a mean of ~2 nm. In comparison to the PDDA synthesis route, Fig. 5d shows that metal precursor impregnation routes followed by reductive annealing yields carbon-supported alloy particles with clearly wider particle size distributions. Further inspection of Fig. 5d showed that PtCu3 particles prepared using impregnation/reduction exhibited very large, unalloyed pure Cu particles in accord with their X-ray diffraction profile (see previous paragraph). The TEM analysis confirms that the polymer-assisted polyol synthesis method is able to produce highly dispersed base-metal-rich nanoparticles with narrow size distribution.

**OBR electrocatalysis of PDDA-Pt-Cu alloy particles.**—Dealloying of Pt–Cu catalysts.—After synthesis PDDA-stabilized Pt–Cu particle electrocatalysts were cast into an aqueous Nafion containing ink, pipetted onto a glassy carbon disk electrode and electrochemically tested in a rotating disk electrode configuration in perchloric acid. The catalyst particles were initially immersed into the nitrogen purged acid electrolyte under potential control (E = 0.05 V/RHE) preventing an uncontrolled dissolution and dealloying of Cu from the alloy particles. Controlled Cu dealloying was subsequently achieved during cyclic voltammetry between 0.05 V and 1.1 V/RHE. Figure 6 shows the initial three cyclic voltammograms for carbon-supported PtCu (Fig. 6a) and PtCu3 (Fig. 6b) alloy particles. For both materials, Cu dissolution in the anodic scan commenced at ~0.3 V/RHE and extends up to an electrode potential of 0.55 V/RHE and 0.7 V/RHE for the PtCu and the PtCu3 catalyst,
respectively. No Cu redeposition was observed on the cathodic scans. The Cu dissolution peak height on subsequent cycles 2 and 3 is clearly reduced, suggesting the gradual removal of alloyed Cu atoms from the surface of the alloy particles.

The observed Cu dissolution/deposition behavior is consistent with earlier reports by Markovic et al. and Ross on underpotential-deposited (UPD)-Cu stripping from Pt single-crystal surfaces. UPD-Cu monolayers deposited on pure Pt exhibit a Cu stripping peak at 0.7 V/RHE under the conditions used here (see Fig. 4 in Ref. 63). Dissolution of Cu atoms deposited on Cu (bulk Cu) commences at around 0.3–0.4 V, in accordance with the Cu standard electrode potential. Cu electrodeposition peaks were only observed at Cu concentrations at or above 10^{-6} mol/L Cu^{2+} ions in the electrolyte. Estimation of the maximum Cu^{2+} concentration due to Cu dissolution in the current experiments resulted in an upper limit of 10^{-7} mol/L Cu^{2+} in the case of complete Cu loss; that is, it is below the redeposition threshold and therefore explains the absence of any discernible redeposition peaks in Fig. 6.

Pugh et al. reported on anodic polarization studies of arc melted Cu-rich (70–80 at% Cu) Pt–Cu alloy samples. He reported on a broad Cu dissolution peak of ~0.3 V/RHE and another one at 0.6–0.8 V/RHE. Consistent with the current results, Cu dissolution peaks around 0.3–0.4 V were caused by pure Cu crystallites or by surface-segregated Cu behaving like bulk Cu, while the dissolution process around 0.6–0.8 V/RHE reflects the Cu dissolution from the alloy surface. Pugh et al. further reported on the selective dissolution of Cu layers from up to a 30 nm depth inside the alloy during the very first anodic potential scan. This underscores the enormous amount of surface atomic material that is affected by electrochemical dissolution of Cu-rich alloy materials. The broad multipeak dealloying features observed in the current study can be explained as follows: The nanoparticle catalysts consist of a distribution of alloy particles with varying size and slightly varying Cu content. Because normal electrode potentials of surface atoms of nanoparticles strongly depend on the particle size (Gibbs–Thomson effect) and composition, the Cu dissolution features are smeared out over a large potential range, with Cu in Cu-rich domains dissolving at more cathodic potentials (starting at 0.3 V/RHE), and Cu from Pt-rich domains dissolving at more anodic potentials (0.4–0.7 V/RHE). Consistent with its higher overall Cu atomic content, the dissolution peak currents of the PtCu catalyst in Fig. 6b are markedly higher than those for PtCu.

Cyclic voltammetry of dealloyed Pt–Cu catalysts.— After continued cycling of the Pt–Cu alloy nanoparticles in deaerated electrolyte (~200 cycles), the typical voltammetric profile of a polycrystalline Pt surface emerged (see Fig. 7), in accordance with earlier reports by Pugh et al.
Hahn et al.\textsuperscript{61} on the voltammetric behavior of the Pt–Cu alloy system. The CV profiles suggest that Cu atoms near the particle surface must have, in large part, been removed by the electrochemical pretreatment and that all subsequent electrocatalysis actually occurred on a dealloyed catalytic surface consisting essentially of pure Pt. The tremendous amount of dissolved Cu in Pugh et al.\textsuperscript{65} corroborates this hypothesis. Energy-dispersive X-ray (EDX) analysis confirmed that the overall Cu content of initially ~75 atom % dropped to ~20–30 atom % with significant Cu depletion near the surface. UPD-hydrogen adsorption and desorption regions allowed an estimate of the electrochemically active Pt surface area (ECSA) of the catalysts after double-layer correction, assuming 210 μA cm\textsuperscript{-2} conversion factor for polycrystalline Pt (see Table I).

As for unsupported nanoparticles, pure Pt exhibited the largest surface area, whereas the PtCu and PtCo catalysts showed much reduced surface areas, likely due to particle agglomeration during the initial voltammetric treatment. The carbon-supported Pt and Pt–Cu nanoparticle catalysts, however, (all ~20 wt % Pt) showed all similar surface area (22–26 m\textsuperscript{2}/g\textsubscript{Pt}) with the ECSA of the Pt–Cu/C catalysts being about twice as high as that of the unsupported catalysts. This may indicate that the carbon support stabilizes the particle dispersion and prevents particle agglomeration. Comparing the surface area of the PDDA–Pt particle catalysts with that of a commercial carbon-supported 20 wt % Pt catalyst (E-TEK Inc., Table I) showed that, despite similar mean metal particle sizes, the PDDA–Pt and PDDA–Pt/C catalysts showed only about one-third of the ECSA of the E-TEK Pt/C catalyst (22 m\textsuperscript{2}/g\textsubscript{Pt} and 26 m\textsuperscript{2}/g\textsubscript{Pt} for the alloys compared to 72 m\textsuperscript{2}/g\textsubscript{Pt} for E-TEK Pt/C). Residual amounts of PDDA most likely cover portions of the particle surface and thereby reduce the catalytically available surface area. Although this does not affect the intrinsic alloy activity (see later discussion), it can significantly affect mass-based activity figures as shown next. Other than blocking parts of the nanoparticle surface, the positively charged residual PDDA polyelectrolyte may also result in somewhat reduced proton conductivity in the immediate vicinity of the alloy particles due to electrostatic interactions with protons and sulphonate groups of Nafion polymer. A significant impact on the measured intrinsic activity, however, is unlikely in the present rotating disk electrode configuration, where convective transport is corrected for and in-film transport effects are generally negligible due to the thin catalyst electrode film.\textsuperscript{6,68}

**ORR activity.**—Figure 8 shows the anodic potential sweeps of carbon-supported PDDA–Pt–Cu nanoparticles in oxygen-saturated acid electrolyte. A diffusion-limited oxygen reduction current of about ~6 mA/cm\textsuperscript{2geo} at 1600 rpm is consistent with earlier ORR measurements in this configuration.\textsuperscript{5,6,29} The anodic sweep profile demonstrates a significant anodic shift in the ORR half wave potential for the Cu-rich PtCo alloy particles associated with a considerably earlier onset of the ORR in the cathodic direction. The inset reports the corresponding Tafel plots in the kinetically controlled potential region using surface-area-specific ORR current densities on the x-axis (μA/cm\textsuperscript{2}). Specific current densities (activities) are calculated by dividing mass transport-corrected kinetic ORR activities by the ECSA considered a measure of the intrinsic catalytic activity independent of surface roughness and particle size.\textsuperscript{26,31} All nanoparticles showed a Tafel slope in the range of ~52 mV/decade to ~70 mV/decade, which is close to the previously reported Tafel slope of about ~60 mV/decade to ~70 mV/decade on Pt alloy surfaces.\textsuperscript{5,26,29,31} The dealloyed PDDA–PtCu\textsubscript{3} electrocatalyst exhibited a significant improvement of ~three times in intrinsic ORR activity over the PDDA–Pt as well as the commercial Pt standard. De-alloyed PDDA–PtCu\textsubscript{3} catalysts hence achieved similar intrinsic ORR activity enhancements as conventional Pt-rich alloy systems, such as PtCo electrocatalysts.\textsuperscript{31} Pt–Co alloy catalysts,

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrochemical surface area (m\textsuperscript{2}/g\textsubscript{Pt})</th>
<th>Surface-area-based (specific) activity (μA/cm\textsuperscript{2})</th>
<th>Pt mass-based activity (A/mg\textsubscript{Pt})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDDA–Pt/C</td>
<td>22</td>
<td>243</td>
<td>0.053</td>
</tr>
<tr>
<td>PDDA–PtCu/C</td>
<td>25</td>
<td>260</td>
<td>0.064</td>
</tr>
<tr>
<td>PDDA–PtCu/C \textsuperscript{a}</td>
<td>26</td>
<td>615</td>
<td>0.157</td>
</tr>
<tr>
<td>Pt/C\textsuperscript{a}</td>
<td>72</td>
<td>213</td>
<td>0.153</td>
</tr>
<tr>
<td>PtCo\textsuperscript{a}</td>
<td>72</td>
<td>230</td>
<td>0.160</td>
</tr>
<tr>
<td>Pt/C\textsuperscript{33}</td>
<td>65</td>
<td>210</td>
<td>0.160</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Commercial 20 wt % electrocatalyst from E-TEK Inc.
considered one of the most active Pt alloy ORR systems, have of-
erred ORR specific activity enhancements of about two to three
times over their corresponding pure Pt standards.5,6,14-16,19,29,31,72,73

An ORR electrocatalyst with a four times activity enhancement over
Pt, however, is currently needed to meet the cost and activity target for
automotive PEMFC cathodes.31,74 Based on the present results, we
suggest that PDDA-free dealloyed Pt–Cu nanoparticles may rep-
resent a suitable catalyst system to achieve surface-area-based and
Pt mass-based ORR activities up to and beyond a fourfold improve-
ment compared to pure Pt.30,60,55,76

The relatively low ECSAs of the PDDA-stabilized particles sug-
gest that residual amounts of PDDA are still severely compromising
the available surface area for ORR electrocatalysis and, therefore,
the absolute measured ORR activity in A/cm². As a result of this,
the Pt mass based ORR activity of the PDDA–Pt/C is about three
times smaller than that of a commercial Pt/C catalyst. Owing to
their intrinsic threefold more active behavior, the PDDA–Pt/C nanoparticles showed a Pt mass activity comparable to that of the
commercial Pt/C catalysts.

**ORR electrocatalysts by dealloying of Cu rich pre-
cursors.—** The presented data show that a selective dissolution of
Cu-rich single-phase Pt–Cu precursor catalysts results in more effi-
cient surface electrocatalysts. Surface roughening during potential
hydriding has previously been described in the electrocatalysis
literature.77 However, increase in surface area by roughening should
do not affect the surface-area normalized specific activities shown in
Table II. Hence, roughening can be ruled out as primary enhance-
ment mechanism.

Dealloying of a non-noble metal component (say B) from a noble
metal (say A) binary alloy A-B (for instance, in the Ag–Au or the
Cu–Au systems) has extensively been investigated in the corrosion
community.7-8,85 It is well known that under certain conditions, se-
lective dissolution of atoms B in combination with rapid surface
diffusion and Ostwald ripening of atoms A can produce highly rami-
ﬁed three-dimensional porous structures of the noble
element.79,81,86,87 The evolution of nanoporosity in these systems is a
self-organized processed and not related to a preformed, hidden
porous structure of the precursor. For the dissolution at a constant
electrode potential to be a self-sustained process, however, and
to proceed deep into the bimetallic material, a critical com-
positional threshold, the so-called dealloying threshold, must be met
by the precursor material. Only above its compositional dealloying
threshold will metal atoms B be exposed to the external electro-
lyte for extended period of times. Below the dealloying threshold, noble
metal A will be blocking all further dealloying. This argument im-
plies that there is a point in time during the dealloying process
where the threshold is crossed and the process comes to a halt. This
is important in the context of electrocatalyst stability because it
means that dealloyed electrocatalysts will attain a point where fur-
ther loss of base metal will be suppressed. Conversely, any given
stochiometry of the bimetallic A-B precursor (up to an upper limit
in the noble metal component) is associated with a “critical poten-
tial” at which self-sustained dealloying sets in Ref. 65 and 81. The
critical potential is naturally located somewhere between the stan-
dard electrode potentials of metal A and metal B. Sieradzki et al.79,82-85
find strong evidence that the dealloying process follows a percola-
tion model based on the sharp onsets in the dissolution currents.

In the context of a modification of the surface electrocatalytic
properties of alloy surfaces, it is the unique characteristics of the
final A-rich (which is Pt-rich in our experiments) catalytic surface
that determine the origin of the observed enhancement. The precise
mechanism of dealloyed Pt alloy catalysts is unclear at the present
time and more in-depth surface characterization of dealloyed Pt
surfaces is needed. However, a purely surface-area-based enhancement
effect can be ruled out based on the H adsorption/desorption surface
area measurements of the dealloyed catalysts. Dealloyed carbon-
supported Pt–Cu electrocatalysts exhibit surface-area increases of
about 15–20% over the pure Pt standards (see Table I), yet this
increase is insufficient to account for the observed activity improve-
ments of three times. Furthermore, specific activity data, as reported
in Fig. 8 and Table II, take surface area changes already into con-
sideration. Electronic structure modification,14-16 caused by base
metal atoms in the first and second catalyst layers also appear un-
likely because the electrochemical dealloying process effectively re-
moves all Cu atoms to a depth of multiple atomic layers.64,65 Be-
cause ensemble effect can be ruled out based on the ORR
mechanism on Pt, there remain mainly geometric effects. Preferred
exposure of favorable crystal planes, the formation of favorable Pt
interatomic distances in the remaining essentially pure Pt surface, or
the formation of a very defect-rich Pt surface is likely to play a key
role in the observed catalytic activity enhancements of dealloyed
alloy nanoparticles.

**Conclusion**

Highly dispersed carbon-supported Pt–Cu nanoparticle electro-
catalysts with very high Cu content were synthesized using a modi-
fied polyol process in the presence of the polyelectrolyte PDDA.
The synthesis route enabled the preparation of single-phase alloy
particles with narrow size distribution at reaction temperatures be-
low 200°C without any pure base metal residuals. The observed
alloy uniformity in combination with a small mean particle size
makes this process superior to conventional impregnation/reductive
annealing synthesis methods, when base metal rich (>50 atom %
metal) is concerned. PDDA-stabilized PtCu/C nanoparticles
exhibited Cu dealloying/dissolution upon electro-
chemical treatment in acid electrolyte, which resulted in the for-
formation of a Cu-depleted active catalyst phase. ORR activity measure-
ments indicated that dealloyed Pt–Cu catalysts possess great
potential for significant activity improvements beyond the current
state-of-the-art by a factor of three times.

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