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Electrocatalysis: theory and experiment at the interface

Guest Editor: Andrea Russell

Editorial

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Voltammetric surface dealloying of Pt bimetallic nanoparticles: an experimental and DFT computational analysis

Peter Strasser,† ac Shirlaine Koha and Jeff Greeleyb

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Voltammetric dealloying of bimetallic platinum–copper (Pt–Cu) alloys has been shown to be an effective strategy to modify the surface electrocatalytic reactivity of Pt bimetallic nanoparticles (S. Koh and P. Strasser, J. Am. Chem. Soc., 2007, 129, 12624). Using cyclic voltammetry and structural XRD studies, we systematically characterize the Pt–Cu precursor compounds as well as the early stages of the selective Cu surface dissolution (dealloying) process for Pt25Cu75, Pt50Cu50, and Pt75Cu25 alloy nanoparticles annealed at both low and high temperature. We also assess the impact of the synthesis conditions on the electrocatalytic reactivity for the oxygen reduction reaction (ORR). To gain atomistic insight into the observed voltammetric profiles, we compare our experimental results with periodic DFT calculations of trends in the thermodynamics of surface Cu dissolution potentials from highly stepped and kinked Pt(854) single crystal surfaces. The modeling suggests a dependence of the electrochemical Cu dissolution potentials on the detailed atomic environment (coordination number, nature of coordinating atoms) of the bimetallic Pt–Cu surfaces. The DFT-predicted shifts in electrochemical Cu dissolution potentials are shown to qualitatively account for the observed voltammetric profiles during Cu dealloying. Our study suggests that metal-specific energetics have to be taken into account to explain the detailed dealloying behavior of bimetallic surfaces.

1. Introduction

Over 2000 years ago, pre-Columbian goldsmiths of the high cultures of Andean South America developed simple surface processing technologies in order to change the properties of metal alloys.2 They were interested in changing the appearance of Au-containing metal alloys to make them appear as if they consisted of pure gold. To achieve this, they invented two techniques: surface metal galvanic displacement and surface metal depletion gilding.2,3

Surface metal galvanic displacement consisted of treating thin polished Cu metal sheets in neutralized heated baths of Au salts, which were prepared from metallic Au by dissolution in corrosive mineral mixtures.2 The Cu sheets were uniformly coated with a thin layer of Au and appear as if they consisted of pure Au: an affordable strategy for impoverished royal families to dress in gold, which, in the then cultural attitude, represented descent from the sun.

The Surface metal depletion technology started with bimetallic ingots of a less noble (Cu) and a more noble metal (Au), known as ‘tumbaga’, which were repeatedly subjected to cold-treatments, annealing, and pickling cycles in order to enrich the surface with copper and then deplete surface copper by chemical dissolution. In this process, the surface of the bimetallic ingot became more and more enriched in Au until it displayed a golden surface.

Both ancient metallurgic strategies for altering surface properties have found their way into modern electrochemical metal surface processing.3–7 While visual appearance was the target property of interest then, the surface electronic structure, and with it, the surface catalytic properties, are the focus of the modifications today.

In order to change the surface electrocatalytic properties of Pt metal alloys, a modern galvanic displacement method has been developed and utilized over the past decade,8–12 which came to be known as the Pt Monolayer Catalyst9 concept. Following the ancient goldsmiths’ strategy, Pt monolayers were deposited onto non-Pt substrates using galvanic displacement of layers of surface Cu atoms (Fig. 1a). The resulting catalysts have shown improved intrinsic surface electrocatalytic activity for the electroreduction of oxygen at much reduced Pt content; they represent one of the most promising new catalyst classes for fuel cell cathodes. Vukmirovic et al.9 reviewed the Pt monolayer concept in detail and pointed out its structural and catalytic characteristics.

Herein, we report an experimental and DFT computational study of a modern voltammetric depletion gilding method designed to deliberately change the electrocatalytic surface reactivity of Pt alloy catalysts for the electroreduction of oxygen (ORR)1,13–16. We selectively dissolve Cu atoms (voltammetric dealloying) from the surface of Pt-Cu bimetallic compounds until a multi-layer Pt-rich shell region has formed (Fig. 1b). While the dealloying of a less noble component from
bimetallic alloys has been investigated on flat surfaces, such as alloy single crystals, we focus on the initial stages of Cu dealloying from nanometer-sized alloy particle ensembles. Metal dealloying from alloy nanoparticles is a poorly understood research area, yet it has tremendous importance for the understanding of high-surface area alloy catalyst degradation in electrocatalysis.

We found Cu dealloying from Pt–Cu bimetallic alloy nanoparticle precursors to result in very active ORR catalysts.1,17 We investigate the voltammetric profiles of Cu dissolution during the early stages of the dealloying process and correlate the voltammetry with structural alloy phase characteristics at various Cu contents and synthesis conditions. We combine our experimental results with computational DFT predictions of metal-specific energetics and assess their impact on the Cu dissolution potentials.

2. Experimental methods

Preparation of the alloy catalysts

Carbon supported Pt–Cu alloy nanoparticle electrocatalysts of stoichiometries Pt25Cu75, Pt50Cu50, and Pt75Cu25 were synthesized via a liquid salt precursor impregnation method reported earlier. Measured amounts of a Cu nitrate (Cu(NO3)2 3H2O, Aldrich) were dissolved in de-ionized water (> 18.2 MΩ, Milli-Q® gradient system, Millipore Inc.). The precursor solutions were then added to a weighted amount of commercial carbon-supported Pt nanoparticle electrocatalyst (Tanaka Kikinzoku Inc.) with a Pt weight loading of about 30 wt%. The mixtures were then ultrasonicated with a sonifier horn (Branson 150, level 2) for 1 min and then frozen in liquid nitrogen for 5 min. Subsequently, the frozen samples were freeze-dried (Labconco) for 24 h and annealed in flowing hydrogen/argon mixtures in a flow furnace (Lindberg Blue) to a temperature of 600 and 950 °C. The annealed powders were stored in a Nalgene® desiccator, with continuous nitrogen gas flow, for future use. The resulting Pt loadings of the Pt–Cu catalysts ranged from 22 wt% to about 30 wt%.

Electrochemical dealloying and ORR testing

A custom-made, three-compartment electrochemical cell was employed for all voltammetric measurements. The working electrode was a commercial glassy carbon rotating disk electrode of 5 mm diameter (PINE Instruments). A catalyst ink was prepared by mixing 20 mg catalyst powder with 16 ml water (Millipore Gradient), 4 ml isopropanol (IPA) and 80 μl of a 5 wt% Nafion® solution (Sigma, #274704), followed by sonication for 15 min at level 2 (Branson 150). A 10 μl aliquot was dispensed onto the 5 mm working electrode disk resulting in a typical geometric Pt loading of about 10 μg Pt/cm². The applied absolute amount of Pt of the catalyst thin films on the RDE varies with stoichiometry of the electrocatalysts and decreased in the order Pt > Pt50Cu50 > Pt50Cu50 > Pt75Cu25.

The reference electrode was a mercury–mercury sulfate electrode. All electrode potentials were subsequently converted into and are reported with respect to the reversible hydrogen electrode (RHE) scale. The counter electrode was a piece of platinum gauze to ensure large surface area. A commercial rotator from Pine Instrument was used to conduct the rotating disk experiment. The electrolyte used was 0.1 M HClO4, prepared by diluting 70% redistilled HClO4 (Sigma, #311421) with de-ionized water. The disk potential was controlled with a potentiostat, BiStat (Princeton Applied Research, Ametek). All measurements were conducted at room temperature. At the beginning of electrochemical measurements, electrocatalysts were immersed into the electrolyte under potential control and held at 0.05 V/RHE until the measurements commenced. Dealloying was conducted in a de-aerated N2 atmosphere electrolyte. The initial three cyclic voltammetric cycles (CVs) were recorded at a scan rate of 500 mV s⁻¹. Thereafter, dealloying was continued for 200 CV cycles over the same potential range at a scan rate of 500 mV s⁻¹, until a stable CV was obtained. Subsequently, another slow CV was recorded at 100 mV s⁻¹. The platinum electrochemical surface area (Pt-ECSA) of the catalyst was determined from that latter CV via the mean integral charge of the hydrogen adsorption and desorption areas after double-layer correction, using 210 μC cm⁻² Pt as the conversion factor. ORR measurements were conducted by linear sweep voltammetry (LSV) from 0.05 V to the open circuit potential (around 1.0 V) at the scan rate of 5 mV s⁻¹. Pt surface area normalized activities were established at 900 mV/RHE, at room temperature by correcting the measured current for mass-transport effects18–20 and dividing the resulting current by the Pt-ECSA. The electrochemical behavior
(CV and LSV) of the Pt–Cu catalysts was compared to a 30 wt% reference platinum electrocatalyst supported on a high surface area carbon support.

### X-Ray diffraction measurements

Laboratory-source XRD (Siemens D5000 θ/2θ Diffractometer) was used to characterize the electrocatalysts structurally. The diffractometer is equipped with a Braun Position Sensitive Detector (PSD) with an angular range of 8°. The Cu Kα source operates at a potential of 35 kV and current of 30 mA. 2θ diffraction angles ranged from 20–70°, scanned with step size of 0.02° per step and holding time of 10–30 s per step. Advanced X-ray Solution (X-ray commander, Bruker AXS) software was used to control the diffractometer from a desktop computer.

The XRD sample holder was a custom-made 3 × 3 cm plexiglass with a 1 cm width × 2 cm length × 1 mm depth well in the center that hold the powder catalyst samples. The catalyst powder was poured into the well and carefully flattened to form a smooth surface, flushed with the surface of the plexiglass.

All XRD diffraction patterns were analyzed using Jade (MDI). Each peak profile of each reflection was obtained by a non-linear least square fit of the Kα2 and background corrected data. Instrumental broadening was determined using an alumina standard under identical measurement conditions. Particle sizes were estimated using the observed line broadening and Scherrer equation at several fundamental reflections. Compositions of Pt–Cu alloys obeyed Vegard’s law21,22 which states that the composition of an alloy is directly proportional to the lattice constant of the alloy with respect to those of its components.

### 3. Theoretical and DFT computational models and methods

The DACAOPO code23 was used for all total energy calculations in this study. The Pt(854) surface was modeled with a 40-atom unit cell periodically repeated in a super cell geometry of 4.02 Å is in reasonable agreement with the experimental value of 3.91 Å.24 The unit cell geometry is such that either three or four metal layers (depending upon the location on the slab surface and the number of surface atoms that have dissolved) perpendicular to the (111) terraces are employed; the top layer of Pt atoms is substituted with Cu, and Cu atoms are sequentially removed to simulate Cu dissolution (see also section 4.4). The calculations are fully converged with respect to the number of metal layers included; removal of the bottom layer of Pt atoms, and subsequent recalculation of the differential binding energies of surface Cu atoms at high coverages (>0.69 ML), shows average differential BE changes of less than 0.02 eV (the actual differential BE changes calculated were 0.011, −0.006, 0.024, and 0.037 eV for dissolution from slabs with 1, 0.92, 0.85, and 0.77 ML of adsorbed Cu atoms, respectively); these values are well within the accuracy range associated with standard DFT calculations. The top (Cu) layer of the slabs is relaxed until the total force on all atoms is less than 0.04 eV Å−1 in any Cartesian direction. Interpolation of dipole corrections are not included in the reported results.13,25 Ionic cores were described by ultrasoft pseudopotentials,25 and the Kohn–Sham one-electron valence states were expanded in a basis of plane waves with kinetic energy below 340 eV; a density cutoff of 500 eV was used. The surface Brillouin zone was sampled with a Chadi-Cohen 6(1×1) k point grid. The convergence of the total energy with respect to the cutoff energies and the k point set was confirmed. The exchange–correlation energy and potential were described by the generalized gradient approximation (GGA-RPBE).23 The self-consistent RPBE density was determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states (kBT = 0.1 eV), and Pulay mixing of the resulting electronic density.26 All total energies were extrapolated to kBT = 0 eV.

The approach for modeling the thermodynamic aspects of metal dissolution on surfaces at standard ion concentrations has been described previously27 briefly, the raw, DFT-derived total energies are corrected for electrode potential effects; the latter effects are estimated by referencing the potential to the standard hydrogen electrode. The dissolution potential of bulk copper,24 Uc, is taken as an empirical reference point, and all shifts in dissolution potential due to changes in the surface chemical environment are referenced to this value. The resulting expression for the total free energy of the Cu atoms on the Pt(854) substrate, neglecting surface entropy effects, is:

\[
G(N_{\text{Cu}}, U) = E_{\text{slab, } N_{\text{Cu}}} - E_{\text{clean}} - (E_{\text{bulk, } \text{Cu}} + 2(U - U_c))N_{\text{Cu}},
\]

where \(N_{\text{Cu}}\) is the total number of Cu atoms per unit cell on the Pt(854) surface, \(E_{\text{slab, } N_{\text{Cu}}}\) is the total, DFT-derived energy of the slab with adsorbed Cu atoms, \(E_{\text{clean}}\) is the Pt(854) energy with no adsorbed Cu, and \(E_{\text{bulk, } \text{Cu}}\) is the cohesive energy of bulk Cu. Implicit in this expression is the assignment of a value of 0 to the free energy of the clean Pt slab (with no adsorbed Cu atoms). In all cases, \(E_{\text{slab, } N_{\text{Cu}}}\) refers to the most stable arrangement of Cu atoms at the indicated value of \(N_{\text{Cu}}\); test calculations demonstrate that these most stable arrangements are associated with removal of Cu atoms from the Cu kinks (removal of Cu atoms from terraces or step edges is less energetically favorable). We note that no corrections for potential-induced electric field effects are included in the calculated free energies; such effects have been shown to have a negligible impact on the thermodynamics in computational studies of the oxygen reduction reaction.28 Finally, in eqn (1), it is assumed that two electrons are transferred to the substrate for every copper ion that dissolves; this choice of this charge state is motivated by the fact that Cu2+ ions dissolve at lower potentials than Cu\(^{+}\) ions.24,29

### 4. Results

#### 4.1 ORR electrocatalysis of dealloyed Pt–Cu bimetallic alloy nanoparticles

Six Pt–Cu bimetallic precursor alloy particle catalysts—three different stoichiometries (Pt25Cu75, Pt50Cu50, Pt75Cu25) at two different annealing temperatures (950 and 600 °C)
Table 1  Comparison of nominal and final compositions, Pt mass based catalytic ORR activities (at 900 mV/RHE), surface area normalized ORR activities (at 900 mV/RHE), and surface areas of Pt–Cu alloy nanoparticle electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt (at.%)</th>
<th>Cu (at.%)</th>
<th>Annealing temperature (°C)</th>
<th>Specific activity (µA cm⁻²)</th>
<th>Pt mass activity (mA g⁻¹ Pt)</th>
<th>Surface area (m² g⁻¹ Pt)</th>
<th>Composition after electrochemical dealloying (at.%)</th>
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<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>75</td>
<td>600</td>
<td>643.77</td>
<td>0.53</td>
<td>88.51</td>
<td>79</td>
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<tr>
<td>2</td>
<td>25</td>
<td>75</td>
<td>950</td>
<td>787.68</td>
<td>0.35</td>
<td>45.16</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
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<td>50</td>
<td>600</td>
<td>595.96</td>
<td>0.51</td>
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<td>50</td>
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<td>233.85</td>
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</table>

(see Table 1)—were electrochemically dealloyed and subsequently subjected to slow anodic potential sweeps in oxygen saturated electrolyte in order to characterize their intrinsic oxygen reduction reaction (ORR) activity. Fig. 2 shows the anodic potential sweeps of the dealloyed catalysts in oxygen-saturated electrolyte. The flat portions of the sweep curves for potentials below 0.8 V/RHE indicate a diffusion-limited regime. For increasing Cu content of the precursor, the steep portions of the curves are significantly shifted to higher electrode potentials compared to the pure Pt standard catalyst (dashed curve), indicative of an enhanced electrocatalytic reaction rate for ORR (reduced overpotential) on dealloyed Pt–Cu surfaces. Combined with the Pt amounts of the alloy catalysts in the RDE film, a kinetic analysis resulted in a 4–5 fold increase in the Pt-mass normalized ORR reactivity for the Cu-richest low temperature catalyst compared to the established 0.10 A per mgPt of pure Pt at 0.9 V/RHE 30 (see Table 1). This dramatic increase is in accord with previously reported RDE measurements of dealloyed Cu-rich Pt–Cu nanoparticle catalysts.1 With increasing Pt content of the precursor material, the observed Pt mass activity dropped to values reported earlier for Pt rich alloys such as Pt₇₅Ni₂₅ or Pt₇₅Co₂₅ 31–35 Catalysts prepared at high temperatures generally showed reduced Pt mass based ORR activity.

Table 1 and the inset of Fig. 2 also report the measured values of the Pt-ECSA and the Pt-ECSA normalized ORR activities of the three dealloyed catalysts at 0.9 V/RHE. The Pt₇₅Cu₂₅ catalyst prepared at 950 °C exhibited an almost 4 fold intrinsic activity increase over pure Pt, in line with earlier reports of this catalyst class.1,15,17,36 Low temperature Pt₅₀Cu₅₀ and Pt₇₅Cu₇₅ catalysts showed slightly smaller activities, while both Pt₅₀Cu₂₅ and the high temperature Pt₇₅Cu₂₅ only showed a 1–2× increase in specific activity, similar to other Pt rich catalysts.30–32,37–49 The electrochemical surface areas of the dealloyed catalysts indicate that none of the catalysts showed a significantly increased surface area compared to a standard carbon-supported Pt with about 77 m². To the contrary, the higher annealing temperature led to a serious decrease of Pt-ECSA due to particle sintering.

4.2 Structural characteristics of Cu rich Pt–Cu bimetallic alloy nanoparticles

To gain insight into the compositional and structural characteristics of the Pt–Cu alloy precursor nanoparticle electrocatalysts, we performed X-ray diffraction studies of all six alloys prior to dealloying.

Pt₇₅Cu₂₅. Fig. 3a and b show the measured profiles of the Pt₇₅Cu₂₅ particles over the 2θ range of the fundamental (111) and (200) peaks of Pt and Cu annealed at low and high temperatures, respectively. The broad peaks around 2θ = 41.9° and 2θ = 48.5° envelop the (111) and (200) reflections of fcc Pt–Cu bimetallic alloy phases.50,51 The absence of superlattice peaks at lower angles confirmed the presence of disordered fcc Pt–Cu alloys. Given the alloy nanoparticle ensemble, the broad alloy phase peaks indicate the presence of multiple Pt–Cu bimetallic fcc phases. In fact, as shown in Fig. 3a, the broad (111) peak was fit using two distinct peaks at 2θ = 42.3° and 2θ = 40.9°, representing two distinct Pt–Cu alloy phases. Furthermore, the low temperature sample shows sharp peaks around 2θ = 43.3° and 2θ = 50.5°, representing the (111) and (200) reflections of a face-centered cubic (fcc) Cu phase. Vegard’s law, which establishes a linear relationship between the unit cell parameter of a bimetallic alloy and its composition, provides an excellent model to predict trends in the composition of crystalline Pt–Cu bimetallic alloy phases based on their peak position.21,22,52

The XRD peak analysis of
the Pt75Cu25 nanoparticles thus revealed that low-temperature annealing (600 °C) resulted in incomplete alloying of Pt and Cu atoms, with excess Cu atoms forming large pure Cu particles. Coexisting with the pure Cu phase are multiple Pt–Cu alloy phases with varying compositions, some of which must consist of a Pt content of > 25 atomic % in order to meet the overall stoichiometry of Pt75Cu25. The high-temperature catalyst in Fig. 3b, however, shows no sign of excess Cu. The fundamental fcc (111) reflection exhibits a much smaller full peak width at half maximum (FWHM). A peak fit of the (111) reflection still required at least two different individual peaks (Fig. 3b), suggesting the presence of more than a single alloy phase. Yet, overall, annealing at 950 °C clearly leads to an improved alloying between Pt and Cu atoms.

Pt50Cu50. Fig. 3c and d show the structural XRD profiles of the Pt50Cu50 alloys annealed at 600 °C and 950 °C, respectively. As with Pt75Cu25, broad reflections for the low-temperature catalyst indicated small particles and/or multiple alloy phases. The low temperature profile was successfully fit with two distinct (111) and (200) peak couples, suggesting the presence of at least two bimetallic alloy phases. The high temperature material profile, on the other hand, suggested the presence of a rhombohedral Pt50Cu50 Hongshiite phase53–56 (PDF file 00-042-1326, space group: R3m, unit cell parameters a, b = 1.070 nm, c = 1.319 nm). Consistent with our measurements, this phase exhibits an intense (006) reflection at 2θ = 41.01° and a (404) reflection at 2θ = 47.9°. Within our probed angle range, the phase is uniquely identified by its characteristic (205) and (241) reflections at 2θ = 39.2° and 2θ = 52.6°, respectively. These latter two peaks are located at angles outside the range between the fundamental (111) and (200) reflections of pure Pt and pure Cu phases; hence, they cannot be assigned to any disordered Pt–Cu bimetallic alloy phase which would show its (111) and (200) reflection in between those of the two pure metals.

Pt75Cu25. Finally, Fig. 3e and f depict the diffraction profile of the Pt75Cu25 alloy nanoparticle electrocatalyst annealed at low and high temperatures, respectively. As expected, the low temperature profile exhibits broader peaks associated with smaller alloy nanoparticles.50 However, both profiles can be fit very well with one single Voigt-type peak, suggesting a relatively homogeneous alloying in the Pt-rich composition range. No sign of excess pure Cu was seen in either the low or the high temperature alloy samples.

### 4.3 Cyclic voltammetric behavior during Pt–Cu dealloying

This section focuses on both the early stage and the final stage of the catalyst dealloying process. Catalyst dealloying is typically performed prior to ORR testing in deaerated electrolyte by voltammetric treatment of the bimetallic precursors. Fig. 4a–f reports the initial cyclic voltammetric cycles of all six Pt–Cu catalysts of interest.

Pt75Cu25. The first cyclic voltammograms (CVs) of the Pt75Cu25/600 °C catalyst (Fig. 4a) show no hydrogen adsorption between 0.05 and 0.3 V, suggesting a very Cu-rich precursor surface. A strong anodic current onset is observed at around 0.25 V, forming a very broad anodic multi-peak band stretching from 0.25 to 0.85 V with three individual peak maxima at 0.4, 0.58, and 0.7 V. This broad anodic current peak represents surface Cu dissolution from the as-prepared precursor bimetallic surface. On the cathodic portion of the first scan, a number of reduction peaks were observed at 0.6, 0.4 and 0.25 V, the latter two of which are likely associated with redeposition of some Cu-ions from solution onto the interface. On the anodic portion of the second and third CV, the broad peak band gave way to a two-peak profile at 0.35 and 0.7 V. On the cathodic direction, the reduction peak currents gradually decreased, and the initial three-peak profile turned into a single reduction peak around 0.65 V. The third CV shows some oxidation of underpotentially deposited hydrogen in the 0.1–0.3 V range, indicating the onset of the exposure of Pt surface atoms, even at these very low potentials. The voltammetric cycling was then continued until a time-stable CV was obtained. The final recorded cyclic voltammogram of the Pt75Cu25 is shown in Fig. 4a as well (solid line). The final profile strongly resembles that of a pure Pt catalyst surface with a well-developed, underpotentially-deposited (upd) hydrogen ad/desorption region and the formation of oxygenated surface species at anodic potentials.
>0.80 V. The final CV suggests that dealloying led to an almost pure Pt catalyst surface by gradual removal of Cu atoms from the alloy particles.

The first three CVs of the Pt$_{25}$Cu$_{75}$/950 °C (Fig. 4b) exhibited a distinctly different peak profile upon dealloying. While the onset potential of the Cu dissolution again occurred around 0.25 V with a current peak maximum at 0.4 V, there were no Cu intermediate dissolution current peaks in the 0.4–0.8 V range. Another current peak maximum was observable at 0.8 V on the first scan. The first cathodic sweep was similar to that of the low temperature material with a pronounced peak around 0.65 V and smaller ones at 0.4 and 0.25 V. On the second and third cycles, the Cu dissolution decreased in peak current and shifted slightly more cathodically compared to the first cycle. The final CV again resembled a pure Pt catalyst with a small residual peak at around 0.7 V, likely associated with continued Cu dissolution (see Discussion). A clear, yet smaller amount of underpotentially deposited hydrogen was observed to ad- and desorb in the 0.05–0.4 V range.

Pt$_{50}$Cu$_{50}$. The first 3 CVs of the low and high temperature Pt$_{50}$Cu$_{50}$ precursors are shown in Fig. 4c and d, respectively. The behavior and profiles of the two catalysts are very similar to each other and share most of their features. The anodic sweep of the first scan immediately exhibits upd-hydrogen oxidation followed by a relatively small Cu dissolution peak at 0.4 V. Similar to later stages of the Pt$_{25}$Cu$_{75}$ behavior, a second asymmetric Cu dissolution peak appears at 0.7 V during the first CV. Already on the second CV, the dissolution peak near 0.4 V disappeared completely, indicating a limited amount of Cu in the surface region. During the second and third CV, the broad peak at 0.7 V was replaced by a sigmoidally shaped voltammetric feature which gradually decreased in intensity and finally disappeared completely. No significant redeposition peaks were discernible on the cathodic portion of any of the initial CVs. The final CV of Pt$_{50}$Cu$_{50}$ again strongly resembled that of pure Pt, suggesting no residual Cu atoms in the surface. A stark difference between the low and high temperature material consisted in the magnitude of the H upd integrals of the initial and the final time-stable CV. The upd hydrogen integral, typically associated with the surface area of Pt surfaces, was much larger for the Pt$_{50}$Cu$_{50}$/600 °C material than for the Pt$_{50}$Cu$_{50}$/950 °C catalyst, in agreement with the notion that high annealing temperature resulted in larger alloy particles with reduced surface area.

Pt$_{75}$Cu$_{25}$. Fig. 4e and f report the initial 3 CVs of the Pt$_{75}$Cu$_{25}$ precursor. Unlike the other catalysts, no Cu dissolution peak around 0.4 V was observable. Slight Cu dissolution was indicated for the low temperature material by a peak at around 0.7 V, which rapidly dropped in intensity during the second and third cycles. As in the other two cases, the final CV was in large part identical to that of a pure Pt surface, with the high temperature profile showing a drastically reduced H upd integral, suggesting large dealloyed nanoparticles.

4.4 Trends in the thermodynamics of Cu dissolution on Pt–Cu alloy surfaces

The working surface of the Pt–Cu alloy nanoparticles is clearly complex, involving both strong compositional profiles near the surface and a variety of effects resulting from undercoordinated surface sites. To gain insight into the detailed, atomic-level energetic factors influencing the dissolution of Cu in these bimetallic systems, we perform periodic density functional theory calculations. We consider the dissolution of a Cu monolayer from a kinked Pt(854) surface; this model provides atomic-level insight into the effect of defects and other rough surface features on the thermodynamics of Cu dissolution (a detailed discussion of the relationship between the model and the experimental systems is presented in section 5.2).

Table 2 gives the calculated binding energies of Cu atoms to the Pt(854) surface as a function of Cu coverage. These data, corrected for potential effects, are used to plot the surface free energy of different numbers of Cu atoms on the Pt(854) substrate at different potentials (Fig. 5a)–(c)—the potential scale, $U$, is referenced to the experimentally-measured equilibrium potential for Cu$^{2+}$ dissolution from bulk Cu, 0.34 V vs.
The maximum number of Cu atoms considered, 13, is equivalent to a full monolayer of Cu. If kinetic effects are absent, then at a given value of the potential, Cu dissolution will proceed until further dissolution would require an increase in the free energy of the surface. Hence, at a value of $U_{E}\approx 0.34 \text{ V}$, at most a single Cu atom is thermodynamically favored to dissolve. This corresponds to a situation wherein the most easily removed Cu atoms (those at the Cu-rich kink sites—Fig. 5d) are primarily in contact with other Cu atoms; hence, the dissolution potential is little shifted from the dissolution potential of bulk Cu. At higher potentials, more Cu atoms begin to dissolve. At $\sim 0.45 \text{ V}$, a large plateau in the free energy vs. $N_{Cu}$ plot develops; this plateau implies that a significant number of Cu atoms will dissolve at or near a single potential. This single dissolution potential, corresponding to dissolution of Cu atoms from the regions between kinks (Fig. 5e), is analogous to what might be observed in dissolution from flat regions of the Pt–Cu nanoparticles. Finally, at potentials greater than 0.5 V, dissolution of Cu atoms that are strongly bound to Pt step and kink edges (Fig. 5f) becomes thermodynamically favorable. These results are summarized in Fig. 5g, an isotherm of Cu dissolution from the Pt(854) surface. As in earlier subpanels of Fig. 5, the number of Cu atoms remaining on the surface at given potentials is determined by the criterion that further dissolution requires an increase in free energy. We note that, although this isotherm is determined on a bulk fcc Pt crystal, the qualitative trends should remain valid for fcc Pt–Cu bulk alloys of other compositions. We further note that, while this isotherm does not include the effects of surface entropy on the dissolution process, it provides insights into the thermodynamics of Cu dissolution from Pt surfaces.

### Table 2

<table>
<thead>
<tr>
<th>$N_{Cu}$</th>
<th>Differential Cu binding energy/eV</th>
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<td>0.01</td>
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<tr>
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<tr>
<td>2</td>
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<tr>
<td>6</td>
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<tr>
<td>12</td>
<td>−0.62</td>
</tr>
<tr>
<td>13</td>
<td>—</td>
</tr>
</tbody>
</table>


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Fig. 5  Density functional theory analysis of Cu dissolution from the surface of a Pt(854) substrate. (a)–(c) Top views of the Pt(854) surface with 13, 6, and 3 Cu atoms per unit cell, respectively, adsorbed on the surface. The yellow lines in (a) denote the surface unit cell. Cu atoms are shaded ochre, and Pt atoms are shaded silver-gray. (d)–(f) Free energy per unit cell (eV) for different Cu coverages at potentials of 0.34, 0.45, and 0.52 V vs. SHE, respectively; for all potential values, the equilibrium potential for bulk Cu dissolution is taken from standard experimental tables. (g) Isotherm of the most thermodynamically stable Cu coverage as a function of the electrode potential.
As described in an earlier report, the synthesis does not involve any liquid-phase reduction, precipitation, filtration, or other steps where incomplete reaction or materials transfer could occur. As a result, it yields very controlled (average) metal stoichiometries for the final catalysts. The synthesis method employs carbon-supported Pt nanoparticle precursors which are impregnated with Cu salts. Thereby, the pre-existing metallic Pt particles serve as centers for alloy formation; their high dispersion (small mean diameter) keeps the resulting alloy mean particle size small compared to co-impregnation techniques in the absence of structure-directing agents. During the annealing process, Cu ions are reduced to the metallic state and diffuse into the preexisting Pt metal particle lattices, gradually forming uniformly alloyed Pt–Cu alloy lattices. Depending on the desired average Pt to Cu ratio, different amounts of Cu atoms have to diffuse into the preexisting Pt particles. This is where the pronounced sensitivity of this method to annealing conditions arises and accounts for the observed multiphase structure for Cu-rich stoichiometries. Preparation of Pt25Cu75 requires about 10 times as many Cu atoms (compared to preparation of Pt2Cu) to inter diffuse with Pt particles in order to form a uniformly alloyed material.

The synthesis method used here differs from all-liquid precursor impregnation/liquid-phase reduction methods. In these, often assisted by surfactants, metal ions are pre-mixed to achieve atomic proximity and then impregnated onto high surface area supports, followed by reduction and alloying. While the surfactants may provide a means to control the resulting alloy particle size, they are generally difficult to remove afterwards without compromising the particle dispersion. Co-impregnation/ reduction of two or more metal salts in the absence of surfactants generally results in large alloy particles.

Alloy uniformity and phase structure. Alloy nanoparticle ensembles are generally not characterized by discrete properties but exhibit distributions of particle size and composition. For the Pt25Cu75 catalyst, low temperature annealing results in small, yet incompletely alloyed, Pt–Cu particles, as observed in Fig. 3a. Incomplete alloying was obvious from the presence of excess Cu. The broad (111) reflection of the alloy phases (Fig. 3a) also suggested the presence of multiple Pt–Cu phases with different Pt-to-Cu atomic ratios. Annealing at higher temperatures (Fig. 3b) resulted in more uniform Pt–Cu alloys, yet also larger average particles.

In the Pt20Cu30 catalyst (Fig. 3c and d), no Cu fcc reflections are observed, indicating that all Cu has diffused into Pt. While the low temperature phase structure still suggests the presence of multiple Pt–Cu alloy phases, the high temperature profile shows the rarely reported single rhombohedral Hongshite Pt–Cu phase. The small peak at 2θ = 39.2° is a uniquely characteristic reflection of this ordered Pt–Cu alloy phase. In contrast to all other alloy phase reflections in Fig. 3, this peak cannot arise from a disordered Pt–Cu fcc phase, because insertion of Cu atoms into Pt fcc lattices invariably leads to lattice-contracted Pt–Cu alloy unit cells with (111) reflections at larger 2θ compared to the pure Pt (111), at 2θ = 39.7°.

In the Pt75Cu25 catalyst (Fig. 3e and f), even at an annealing temperature of 600 °C, the Cu atoms form uniformly alloyed disordered fcc Pt–Cu alloy phases. Again, with increasing annealing temperature, the mean alloy particle size increases, as seen by a comparison of the FWHM of the (111) reflections in Fig. 3e and f.

ORR activity of Pt–Cu alloys. In earlier reports, we described the significant increase in the ORR activity achieved using dealloyed Pt25Cu75 bimetallic nanoparticle electrocatalysts. Prepared at 600 and 800 °C, the dealloyed Pt25Cu75 catalyst precursors were found to exhibit a 4–6 fold activity advantage over a standard carbon supported 45 wt% Pt nanoparticle catalyst in terms of Pt mass-based (0.4–0.6 A mg−1Pt) and Pt surface area-based activity (700–900 μA cm−2Pt). Similar activity increases were recently also realized in single MEAs under realistic fuel cell conditions. The current results provide insight into the relationship between the ORR reactivity and the Cu content of the electrocatalyst precursor alloy. The compositional data given in the last column of Table 1 evidences that Cu dealloying does occur during voltammetric treatment of the Cu-rich Pt–Cu...
Annealed at 600 °C, the dealloyed active catalysts seem to maintain their high Pt-mass and specific activity, at least up to a Pt atomic ratio of 50% (see Table 1, Catalysts 1 and 3). Annealed at 950 °C, alloy particle growth generally reduced the ESCA which, in turn, reduced the Pt mass activity. The alloy phase uniformity, however, improved and the individual phase compositions approached that of the overall stoichiometry. The Pt25Cu75/950 °C precursor characterized by the largest particle size and by uniform alloying exhibited the highest intrinsic activity after Cu dealloying; this is in agreement with recent MEA measurements of dealloyed Pt25Cu75 catalysts. This suggests that a highly dispersed, uniformly alloyed Pt25Cu75 precursor might result in a very favorable dealloyed catalyst from both a Pt-mass and an intrinsic activity point of view.

The opposite relation between annealing temperature and intrinsic activity was observed for Pt50Cu50. This analysis shows that the alloy phase structure characteristics (ordered, disordered, multi phase or single phase, etc.) significantly impact the catalytic activity of the resulting dealloyed catalysts.

The Pt-rich Pt25Cu75 precursors showed a familiar activity increase of about 2–2.5 × over pure Pt at low annealing temperatures, in line with many previous reports on Pt alloy ORR catalysts with about 75 at.% Pt. The Pt-rich alloys annealed at high temperature (large particles) did not show any activity advantage at all.

To put the observed ECSA-normalized activity values of dealloyed Pt–Cu bimetallic catalysts in perspective with the corresponding activities of extended flat surfaces, we point out that flat Pt and Pt alloy surface exhibit much larger ESCA normalized (specific) ORR activity. Pt-mass based ORR activities are meaningless for extended surfaces. Flat pure Pt shows a specific ORR activity of about 1500 μA cm⁻² Pt⁻¹ while extended Pt alloy surfaces show the familiar 2–2.5 fold enhancement (2000–4000 μA cm⁻² Pt⁻¹).

Selective metal dissolution from flat Pt alloy surfaces for the purpose of improved electrocatalysis was reported as early as 1988 by Paffett et al. The authors investigated the impact of Cr surface dissolution from flat Cr-rich Pt–Cr precursors on the observed ORR activity. They observed significant surface roughening due to Cr dissolution, which led to increases in the absolute (geometric area-normalized) ORR currents. When normalized to the real surface area, however, the ORR activities of Pt–Cr was comparable to that of pure Pt. The authors concluded that the addition of Cr to a Pt surface, and the associated surface roughening, does not provide a substantial benefit for ORR activity. Other reports where dealloyed flat metal surfaces were proposed for use as high surface area interfaces for catalysis and sensing include the work by Ding et al. as well as Liu et al. Both studies emphasize the advantage of nanoporosity derived from flat surfaces for achieving improved catalyst dispersion.

As outlined earlier and confirmed in the present study, the mechanistic origin of the ORR activity improvements of carbon-supported dealloyed Pt–Cu nanoparticle catalysts compared to carbon-supported Pt catalysts is not based on an increased surface area. We believe that the increased reactivity of dealloyed Cu-rich Pt–Cu nanoparticle catalysts lies primarily in the modified geometric and electronic properties of the Pt-enriched nanoparticle shell. This is in analogy to other core–shell type catalyst concepts, such as the “Pt monolayer” particle catalysts reported by Adzic et al. or the “Pt-skin” catalyst concept introduced by Markovic and Stamenkovic. The “Pt monolayer” and “Pt skin” catalysts are characterized by an immediate neighborhood of Pt surface atoms and non-Pt atoms in the second layer, resulting in changes in the Pt–Pt distance on the surface (geometric effects) as well as changes in the electronic structure due to charge transfer (ligand effects). Both effects are convoluted in these catalyst structures. In contrast, tuning the thickness of the Pt enriched shell of dealloyed Pt–Cu particles should, in principle, allow a separation between geometric and ligand effects by isolating geometric effects for thicker shells.

Recently, the hypothesized core-shell structure of our active catalysts was confirmed using anomalous small angle X-ray scattering experiments. Compressive strain in the Pt-enriched particle shell appears to play a critical role in the activity enhancement.

5.2 Experimental and theoretical Cu dissolution potentials

Pt25Cu75. The absence of H upd peaks during the first CV in Fig. 4a and b for the two Pt25Cu75 precursors indicates an essentially pure Cu surface and is in agreement with the tendency of Cu to segregate to the surface of Pt–Cu alloys under thermal treatment. The onset potential of the broad anodic faradic process in Fig. 4a and b in the 0.30–0.35 V range is associated with pure Cu dissolution according to:

\[ \text{Cu(s)} \rightarrow \text{Cu}^{2+} + 2e^- \quad E^\text{c} = +0.34 \text{ V/NHE}. \]  

Formation of Cu(0) species is not favored under the chosen conditions. We suspect that the anodic process represents the dissolution of Cu surface atoms embedded in a Cu environment (Cu bulk atoms) and denote these Cu surface atoms as Cu@Cu. Considering the alloy phase structure discussion above, multi layers of pure Cu are indeed present in the Pt25Cu75/600 °C sample, both in the form of pure Cu particles as well as in the form of surface-segregated Cu layers on top of the Pt–Cu alloy particles for both the Pt25Cu75/600 °C and the Pt25Cu75/950 °C precursor. The behavior of the Cu@Cu atoms is qualitatively similar to that of the first one or two Cu atoms to dissolve from the monolayer on the Pt(854) surface in our theoretical calculations (see discussion below; as noted above, those atoms are primarily in contact with other Cu atoms and are calculated to dissolve at essentially the bulk Cu dissolution potential.

The broad voltammetric Cu dissolution feature stretching from 0.4–0.8 V, with peaks at 0.6 and 0.75 V for the Pt25Cu75/600 °C catalyst, indicates the presence of other Cu surface atoms with distinctly more anodic dissolution potentials. We suspect that, depending on their chemical environment at the atomic scale, their individual corrosion potentials vary over a certain range. Indeed, a direct correlation between the Cu surface atomic environment (local composition,
coordination number, and nature of the coordinated neighboring atoms) of each individual alloy particle and its corresponding local Cu corrosion potential is hypothesized and further supported by our DFT results in Fig. 5.

For the Pt$_{25}$Cu$_{75}$/950 °C material, only Cu@Cu bulk dissolution around 0.35 V and the Cu dissolution around 0.75 V are present. This is consistent with the notion of a more uniformly alloyed nanoparticle ensemble, which shows a narrower particle composition distribution and therefore exhibits more defined corrosion potentials. This is also in excellent agreement with anodic polarization behavior reported by Pugh et al. who monitored the dealloying of arc-melted, flat Pt$_{25}$Cu$_{75}$ surfaces with very well controlled stoichiometries. Pugh’s measurements (Fig. 2 in ref. 7) showed Cu@Cu bulk dissolution around 0.35 V, followed by reduced currents in the 0.4–0.6 V potential range (termed “Passivation” by Pugh); he identified the peak at 0.75 V as the actual Cu dissolution peak from the Pt–Cu alloy. He did not, however, provide atomic insight into the Cu dissolution processes.

A classic single-crystal study by Markovic and Ross of the faradic Cu dissolution and deposition processes on Pt(111) and Pt(100) provides valuable experimental insight into the atomistic processes underlying our measured Cu dissolution behavior. Remarkably, the observed qualitative voltammetric profiles on Pt(111) and Pt(100), as well as the Cu-related peak potentials, are nearly identical to the measured profiles on the Pt–Cu nanoparticles. The surprising correspondence between the structurally complex, compositionally varied nanoparticle surfaces and the structurally well-defined Cu@Pt(111) and Cu@Pt(100) surfaces suggests that reasonably flat regions may exist on our nanoparticles; it may also be true that occasional steps or kinks are present in the single crystal samples. The correspondence also suggests that qualitatively useful insights into the nanoparticle dealloying process can be obtained from our simple Cu@Pt(854) single crystal model.

Markovic and Ross’s combined voltammetric and LEED studies related the anodic peak around 0.35 V to Cu multilayer (Cu@Cu bulk) dissolution, while asymmetric anodic peaks around 0.75 V were unambiguously associated with Cu monolayer upd and Cu monolayer stripping. It follows that Cu atoms sitting on top of pure Pt subsurface layers (denoted here as Cu@Pt) exhibit a significantly more anodic dissolution potential than those sitting on pure Cu surfaces. This observation is completely consistent with our theoretical calculations (showing an increased dissolution potential of Cu atoms on terrace-like Pt(111) regions compared to bulk Cu—Fig. 5e and g) and lends support to our hypothesis that the chemical environment has a significant impact on the detailed metal dissolution profiles. Markovic and Ross further observed that while the Cu@Pt dissolution occurred in a fairly narrow potential range, its formation on the cathodic scan occurs over a broad potential range with multiple peaks at 0.6 and 0.4 V, in line with the observed peak potentials in Fig. 4. Bulk Cu deposition started at around 0.2 V on the single crystals (Fig. 4 and 5 in ref. 83), also in close agreement with the observed cathodic peaks in this study.

The small Cu@Cu bulk dissolution peak present in the Pt$_{50}$Cu$_{50}$ alloys (Fig. 4c and d) indicates that some bulk-like Cu surface atoms must be present, given the absence of unalloyed pure Cu particles. However, the presence of H upd between 0.05–0.4 V also suggests the presence of Pt surface atoms. Segregated Cu therefore appears to be present as islands unable to cover the entire particle surface. Finally, the Cu@Pt dissolution peak around 0.7–0.75 V becomes weaker with increasing Pt content and sharply drops in intensity on the second potential scan, suggesting a rapid depletion of Cu near the surface. As with the 75 at.% Cu materials, continued cycling finally resulted in a pure Pt profile. Finally, the Pt$_{75}$Cu$_{25}$ compositions (Fig. 4e and f) seem to have very little surface Cu initially and show a well-developed H upd peak, even on the first CV scan.

**The critical Cu dissolution potential.** Fig. 6a plots the anodic polarization portions of the initial 3 CVs of the Pt$_{25}$Cu$_{75}$/600 °C alloy particles in a log I–E plot in order to highlight the quasi-constant Tafel Slope of the Cu dissolution onset between 0.2 and 0.4 V. We attempt to provide some insight into the observed dissolution behavior of Pt–Cu alloy nanoparticle Pt$_{50}$Cu$_{50}$, Pt$_{75}$Cu$_{25}$. The small Cu@Cu bulk dissolution peak present in the Pt$_{50}$Cu$_{50}$ alloys (Fig. 4c and d) indicates that some bulk-like Cu surface atoms must be present, given the absence of unalloyed pure Cu particles. However, the presence of H upd between 0.05–0.4 V also suggests the presence of Pt surface atoms. Segregated Cu therefore appears to be present as islands unable to cover the entire particle surface. Finally, the Cu@Pt dissolution peak around 0.7–0.75 V becomes weaker with increasing Pt content and sharply drops in intensity on the second potential scan, suggesting a rapid depletion of Cu near the surface. As with the 75 at.% Cu materials, continued cycling finally resulted in a pure Pt profile. Finally, the Pt$_{75}$Cu$_{25}$ compositions (Fig. 4e and f) seem to have very little surface Cu initially and show a well-developed H upd peak, even on the first CV scan.

![Fig. 6](image-url)
ensembles, such as that described in Fig. 6a, using simple, schematic, anodic log \( I-E \) polarization schemes (Fig. 6b). Such schemes were first discussed by Pickering\(^5\) and later by Sieradzki\(^8,44\) in order to illustrate the observed polarization behavior of flat bimetallic alloy surfaces.

The scheme in Fig. 6b shows the Butler Volmer (BV) dissolution characteristics of bulk Cu and bulk Pt as the left-most (solid) and right-most (dotted) diagonal line, respectively, with their characteristic thermodynamic dissolution onset potential \( E^\circ \) given at the bottom of the graph. Also shown are cartoons of the surface atomic arrangements associated with the two distinct dissolution potentials of pure Pt and pure Cu. The cartoons are to emphasize the impact of the nature of the coordinating atoms surrounding a surface atom to be dissolved; they do not do justice to the effects of coordination number (discussed in our theoretical treatment below), which also impact the dissolution behavior. Cu atoms on Cu atoms (Cu@Cu) result in the Cu bulk dissolution, while Pt surface atoms on top of Pt atoms (Pt@Pt) lead to the Pt dissolution at 1.19 V.\(^8,44\)

In between the two pure metal log \( I-E \) curves, two additional Cu dissolution characteristics are depicted (dashed and solid curves) in Fig. 6b for two different Pt–Cu alloy surfaces with distinct stoichiometry. From dissolution studies on flat surfaces,\(^4,58-60,84\) it is known that the bimetallic alloy stoichiometry below the parting limit correlates with a characteristic critical dissolution potential (\( E_{\text{critical},1} \) and \( E_{\text{critical},2} \) in Fig. 6b) above which major dissolution of the less noble metal component commences (steep portion of curve). Cathodic of the critical dissolution potentials no significant Cu dissolution occurs (flat portion of polarization curve).

A huge body of literature has been dedicated to clarifying the origin and the controlling factors of the critical dissolution potential \( E_{\text{critical}} \) and the associated dealloying processes.\(^3-6,57-60,84-93\) There is even some controversy as to how to best determine the true critical dissolution potential of a bimetallic alloy.\(^8,44\) Experimental and theoretical methods used to characterize and describe the processes around the critical potential include polarization curves, cyclic voltammetry, \( \text{in situ XRD} \), electron microscopy, Monte Carlo simulations, as well as empirical free energy models.

Pickering\(^5\) argued that the critical potential arises from the competition between the surface dissolution rate of the less noble element and its volume diffusion rate to the surface. Past the critical potential, he argues, pitting corrosion sets in and inflicts large-scale damage to the alloy surface.

Sieradzki\(^8,44\) reproduced essential features of bimetallic dealloying curves using kinetic Monte Carlo simulations in 2D and 3D. Based on percolation theoretical arguments, he stressed the competition between the dissolution kinetics of the less noble metal and the surface diffusion of the more noble metal as the controlling factor for the critical dissolution potential; it represents the balance point between roughening and smoothing.

Quasi-atomistic approaches\(^4,60\) to model the critical dissolution potential were reported by Erlebacher and coworkers; these analyses considered the thermodynamic impact of the number of nearest neighbors on the activation energy and rate of metal dissolution and diffusion. The kinetic models were able to capture the evolution of nanoporosity length scales during the bulk dealloying above the critical potential.

Other modeling approaches have considered the thermodynamics of curved surfaces\(^33\) by taking into consideration the Gibbs–Thomson relation or have identified the interfacial energy of two metals as a lumped empirical thermodynamic parameter to model the critical dissolution potential.

We stress that the modeling approaches reviewed above do not consider alloy-specific energetics of intermetallic bond making and bond breaking. Thus, while the models can provide useful insight into the dealloying process and in the evolution of nanoporosity,\(^4\) their general applicability to any given bimetallic alloy system remains unclear. Indeed, Pugh \( et\ al.\)\(^7\) pointed out in his discussion of dealloying in the Pt–Cu system that the inclusion of metal- and site-specific binding energies, that is, the thermodynamics on the atomic scale, might be necessary in order to accurately capture the experimental voltammetric dealloying behavior; below, we discuss the first steps in such a metal- and site-specific theoretical treatment.

Experimental \( \text{in situ XRD} \) investigations of the dealloying processes at the atomic scale to the left and right of the critical dissolution potential was realized by a number of excellent studies by Renner \( et\ al.\)\(^8,9\) in a study on Cu dissolution from Cu\(_{3}\)Au single crystal surfaces, the authors were able to show the formation of a three-monolayer thick Au-enriched passivation layer with inverted stacking at potentials cathodic of the dissolution potentials. Anodic of these potentials, the authors found 12 monolayer thick Au-rich islands, which inherited the inverted stacking of the passivation layer.\(^9\)

While these studies clarified the dealloying mechanism from Cu\(_3\)Au, it is unclear whether these results are equally valid for other bimetallic systems, such as Pt–Cu. A similar study performed with Cu\(_{3}\)Pd\(_{17}\) remained inconclusive whether or not a similar Pd rich passivation layer was formed cathodic of the Cu corrosion potential.\(^9\)

The impact of metal specific binding energies. Our first-principles DFT calculations explicitly incorporate metal-specific binding energies into the treatment of dissolution, thereby permitting us to establish relationships between the detailed local chemical environment (the coordination number and the nature of the coordinating atoms) of the Cu surface atoms and their thermodynamic dissolution potential. As discussed above, although the structural model does not explicitly treat the effects of bulk alloying on dissolution dynamics, it does provide insight into the effect of undercoordinated surface features on the dealloying process, and it is able to qualitatively reproduce certain features of the cyclic voltammograms in Fig. 4.

Our analysis provides a direct link between the binding energy of Cu atoms to the Pt(854) substrate and the dissolution potential. From eqn (1) above, it may be shown that the potential at which surfaces with \( N_{\text{Cu}} - 1 \) and \( N_{\text{Cu}} \) copper atoms, respectively, have equal free energies (i.e., the potential at which at transition between these two states—a dissolution event—will become thermodynamically favorable) is

\[
U - U^\circ = -\frac{1}{2} \left( E_{N_{\text{Cu}}} - E_{N_{\text{Cu}} - 1} - E_{\text{bulk,Cu}} \right)
\]

(3)
where the term in parentheses may be interpreted as the binding energy of a Cu atom to the Pt substrate and can vary with both the coverage of Cu and the structure of the underlying Pt surface; $U^\circ$ is the experimentally determined dissolution potential of bulk Cu. This relationship immediately establishes an atomistic interpretation of the thermodynamic dissolution potential; namely, for Cu atoms that are strongly bound to the Pt substrate and to the neighboring Cu atoms (implying that the term in parenthesis is very negative), the dissolution potential will be shifted to more positive values.

Eqn (3) can be used to interpret the simple isotherm presented in Fig. 5g. Cu atoms that dissolve at potentials near the bulk Cu dissolution potential are bound primarily to other Cu atoms (Fig. 5a). In contrast, the significant number of Cu atoms that dissolve at $\sim 0.45$ V (corresponding to dissolution from Cu on terrace-like Pt(111) regions of the (854) surface—Fig. 5b) are bound to more Pt atoms than to Cu atoms; the higher dissolution potential implies that Cu–Pt bonds are stronger than Cu–Cu bonds (eqn (3)). We note that, although this shift is qualitatively consistent with our experimental CVs (Fig. 4), the quantitative value of the dissolution potential, 0.45 V, is lower than the high-potential peak shown in many of the CVs; this modest quantitative discrepancy may be due to kinetic barriers to Cu atom dissolution (not accounted for in this analysis) associated with rearrangement of water atoms or other related processes, analogous to the modest barriers determined for proton discharge on Pt(111) by Skullason et al. Alternatively, as suggested by Leiva et al., it is possible that small quantities of oxide or other species contaminate the experimental Cu surface in this potential range, thereby rendering dissolution more difficult—although it is important to note that no voltammetric evidence of such species has been found in this or previous work. Finally, the relatively small number of Cu atoms that are bound primarily to Pt steps and kinks show the highest dissolution potentials (Fig. 5c) and, by eqn (3), the strongest binding to the surface.

The theoretical isotherm in Fig. 5g can also be related to the experimental dissolution curves presented in Fig. 4. Each point in Fig. 5g represents the thermodynamic dissolution potential of a chemically distinct type of Cu site on the Pt(854) surface. If, as a first approximation, we neglect interactions between the various sites, and if we consider only the thermodynamic limit of dissolution, then the Cu atoms at each type of site should follow Langmuir dissolution isotherms. Each site would then contribute an approximately Gaussian-shaped peak to the dissolution current, with the peaks centered at the equilibrium dissolution potential of the corresponding site. The net superposition of such peaks is shown in Fig. 7. Although this theoretical curve is clearly a simple superposition to the measured voltammograms, and although, as discussed above, many complex structural and electronic features are likely responsible for these curves and for the critical potential, the curve nonetheless provides insight into some of the voltammetric features, including the multilayer peak at 0.34 V and the shifted underpotential deposition peak at higher potentials. This simple analysis therefore suggests that some features of the curves may be related to simple, atomic-scale changes in the binding energy of Cu atoms to the Pt alloy surfaces as a function of Cu atom coverage.

The simple thermodynamic results presented in Fig. 5 and 7 can also provide qualitative insight into certain features of the Tafel-style dissolution plots in Fig. 6. The second and third curves of that figure represent dissolution of Cu atoms in different chemical environments, analogous to the different types shown in Fig. 5. In Fig. 7, we have treated the current produced by dissolution from such sites by assuming a finite number of Cu atoms at each site, as these atoms are depleted, the current decreases, leading to the Gaussian-type peak shapes. However, if the surface Cu atoms are continuously replaced by Cu atoms from the bulk, as suggested by Pickering in his analysis, there will be no decrease, and continuous current will be produced from each type of site after the thermodynamic potential is reached, as in Fig. 6.

6. Conclusions

(1) We have presented a strategy to modify the surface catalytic properties of Pt bimetals. The strategy is in principle based on the ancient method of 'surface depletion gilding' for changing surface compositions of bimetallic compounds, which dates back over 2000 years to pre-Columbian goldsmiths in Mesoamerica. Our modern flavor of the ancient method uses electrochemical voltammetric sweeps to selectively dissolve less noble alloy components (dealloying), in our case Cu, while the more noble components, herein Pt, remain in the alloy.

(2) We have established detailed qualitative relationships between the synthesis conditions of the Pt–Cu alloy nanoparticle precursors, their structural characteristics and their voltammetric profiles during the early stages of Cu dissolution.

(3) We have shown that dealloyed Pt–Cu alloy nanoparticle electrocatalysts prepared by partial Cu dissolution from Cu rich Pt$_{25}$Cu$_{75}$ precursor alloys exhibited a 4–5 fold ORR activity enhancement on a Pt-mass basis compared to state-of-the-art
pure Pt nanoparticle catalysts. The most active catalyst for the ORR on a ECSA-normalized metric (specific ORR activity) was achieved after surface Cu dissolution from a uniformly alloyed (950 °C annealing) Pt25Cu75 nanoparticle precursor alloy in accordance with recent MEA studies.17

(4) DFT computations of the energetics of Cu adatom dissolution from a (854) model surface yielded a metal- and site-specific correlation between the local atomic environment of Cu surface atoms and their detailed dissolution potential. Cu surface atoms with multiple Cu coordinations dissolved near the thermodynamic bulk Cu potential, whereas under-coordinated Cu surface atoms or Cu surface atoms with primarily Pt neighbors showed higher dissolution potentials.

(4) The combination of experimental data and DFT computational results has corroborated our hypothesis that, in addition to the previously suggested balance between metal dissolution and surface diffusion kinetics, metal-specific interactions on the atomic scale are important controlling factors in the understanding of the onset potentials of Cu dissolution for Pt-Cu bimetallics (critical dissolution potentials). First principles computation of binding energies has revealed that the local chemical environment of surface Cu atoms is a controlling factor for the dissolution onset potentials.

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