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Highly active hydrogen evolution reaction (HER) catalysts formed by energetic Pt_n cluster deposition: Deposition dynamics and the HER mechanism

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Abstract

Mass- and energy-selected Pt_n⁺ ($n \leq 7$) clusters were deposited at variable energies on highly oriented pyrolytic graphite (HOPG) to create highly active electrocatalysts with clusters stabilized by interaction with carbon defects and subplanted Pt atoms. The impact dynamics were studied by Born-Oppenheimer molecular dynamic (BOMD) trajectories, and the physical properties were probed by X-ray photoelectron spectroscopy, low energy He⁺ ion scattering, and a variety of electron microscopy methods. For low deposition energies, the Pt_n deposit onto the HOPG surface, with sticking probability below unity, and aggregate at defects and steps. With increasing deposition energy, the sticking probability initially decreases, then approaches unity as

subplantation and carbon defect creation increase the Pt-surface binding. The activities of Pt_n/HOPG electrodes were studied for the hydrogen evolution reaction (HER) and compared to activities for Pt_n soft-landed on fluorine-tin oxide (FTO) and on Ar⁺-impact-damaged HOPG, as well as the activity of the surface layer of bulk Pt. Geometries and energetics for H atom adsorption and H₂-forming reactions were computed for ensembles of structures identified in the trajectories, and the rate-limiting barriers were found to be low and weakly dependent on the Pt_n size and structure. Consistent with that finding, the HER currents were high and weakly dependent on both deposited cluster size and deposition energy, apart from the highest energies, where much of the Pt is subplanted in electrolyte-inaccessible sites. The HER activities were stable in repeated potential cycling, unless the upper potential ranged into oxidizing conditions. In that case, electrodes with Pt all on the surface were still stable, but electrodes with Pt initially subplanted became more active as Pt emerged into electrolyte-accessible surface sites.

1. Introduction

Because of its high cost, there has been extensive work on developing Pt-free electrocatalysts, despite Pt's high activity¹ for reactions such as the hydrogen evolution reaction (HER). Another approach to reducing the need for Pt in electrocatalysts is to reduce the Pt particle size, increasing the fraction of Pt that is electrolyte-accessible in the particle surfaces, and potentially enabling more efficient reaction due to cluster-size-dependent electronic properties² and the fluxionality^{3, 4, 5} of small clusters under reaction conditions. As a result, there have been studies of HER electrocatalysts based on small, supported Pt clusters or on Pt single atom catalysts, which often also contain small clusters.⁴⁻⁶

We previously showed that sub-nanometer Pt_n clusters deposited on indium-tin oxide (ITO)⁴ and fluorine-tin oxide (FTO)⁵ supports have strongly size-dependent HER activity in acid electrolyte, with Pt atoms being inactive, and activity increasing with cluster size from Pt₁ to Pt₈. For the larger clusters, the mass activity (A/mg_{Pt}) was found to be roughly double that of the surface monolayer of polycrystalline Pt (Pt_{poly}), suggesting that control of Pt_n size and interactions with the electrode support might allow creation of highly active HER catalysts. DFT indicated that the small Pt_n are fluxional under reaction conditions, i.e., their structures evolve under reaction conditions to allow more H atom adsorption *per* Pt atom, compared to the surface of bulk Pt.⁷ Both ITO- and FTO-based electrodes are unstable with respect to metal leaching outside a relatively narrow potential range,⁸ and they are challenging to treat theoretically because the exact surface structure is not well known and large periodic cell sizes are required.

Electrodes with carbon supports are common, and highly oriented pyrolytic graphite (HOPG) provides a model support with well-defined structure that makes accurate modeling more tractable. The electrochemical properties of HOPG have been studied previously, with a particularly useful summary of the structure-property relationships and relation to other carbon sp² electrode materials in a recent review by Unwin *et al.*⁹ As shown below, HOPG is quite inert as an HER catalyst under the conditions studied, but there are several issues that might hamper Pt_n/HOPG electrode preparation, or degrade the electrode stability.

HOPG basal planes are relatively unreactive and metal-HOPG binding is weak, raising the possibility that metal clusters deposited from vacuum onto HOPG might not stick efficiently, i.e., the sticking probability may be below unity. Indeed, Murakami and co-workers^{10, 11} studied sticking and scattering of Ag_n⁺ clusters impacting HOPG at variable energies, observing that the

sticking probability was high only when the deposition energy was high enough to allow processes such as C-C bond scission and Ag subplantation. At low deposition energies, sticking was also reasonably efficient, but at intermediate energies (~ 6 to ~ 20 eV/atom), the sticking probability went through a deep minimum. We address the energy-dependent dynamics of Pt_n deposition on HOPG via experiments and *ab initio* molecular dynamics simulations.

Weak metal-HOPG binding also raises the question of whether supported clusters remain intact, or if they fragment, diffuse, dissolve, and/or sinter to larger aggregates, either upon deposition or under electrochemical conditions. Metal clusters soft-landed on HOPG tend to diffuse and aggregate,^{12, 13, 14, 15} but by increasing the deposition kinetic energy it has been shown that hard-landed clusters can become pinned, i.e., stabilized against diffusion.^{13, 14} For example, Habibpour *et al.*¹⁶ reported that Pd_n ($n = 10\text{--}120$) deposited at 15 eV/atom were stabilized sufficiently to survive use as oxidative dehydrogenation catalysts, with only modest changes in the height distributions measured by post-reaction STM.

Details of the experimental and computational methods are given in the Supporting Information (SI). Briefly, Pt_n/HOPG electrodes were prepared by depositing size-selected Pt_n^+ on HOPG in an ultrahigh vacuum (UHV) system at controlled kinetic energies.^{4, 17, 18} See Figures S1 and S2 for details. All electrodes were exposed to identical Pt fluxes of 1.5×10^{14} Pt atoms/cm², in the form of different size Pt_n^+ . This flux is equivalent to 10% of a monolayer of Pt(111), therefore we refer to such samples as “0.1 ML Pt/HOPG”, however, the actual Pt surface coverages may be lower due to Pt subplantation or non-unit sticking probability. Pt sticking and the fraction of Pt on the surface were characterized by X-ray photoelectron spectroscopy (XPS) and low energy He^+ ion scattering (ISS), respectively, and we imaged the clusters using scanning transmission electron microscopy (S/TEM), cryo-S/TEM, and cryo-TEM. Electrochemistry was studied in a benchtop electrochemical cell.^{4, 5}

Cluster deposition was simulated using multiple Born-Oppenheimer molecular dynamics (BOMD) trajectories, with energies and forces calculated using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional¹⁹ within the generalized gradient approximation (GGA), augmented with Grimme’s D3BJ dispersion correction²⁰ to account for van der Waals interactions. The trajectories were used to identify the most common types of Pt sites created by energetic impacts, and further DFT simulations were then used to estimate the HER activities, using an approach described below. See the SI for details.

2. Results and discussion

The dynamics of Pt_n-HOPG collisions: Sticking and subplantation.

Key questions include the deposition energy dependence of the Pt_n sticking probability on HOPG, the probability of subplantation or other defect creation, the fraction of Pt deposited on or in the HOPG surface layer, the nature of the Pt binding sites, and whether hard-landed Pt_n become pinned on the surface.

The sticking probability, i.e., the fraction of deposited Pt_n that remained on or in the HOPG sample, was estimated by measuring the Pt 4f XPS intensities for a series of samples prepared under different conditions. Each sample had identical Pt exposure (0.1 ML equivalent) in the form of different size Pt_n⁺ at different impact energies. XPS was measured after transfer in air to a Kratos Axis Ultra instrument. A complicating factor is that the largest available XPS analysis area (300 μm $\times$ 700 μm) was considerably smaller than the cluster spot, defined by a 2 mm diameter mask positioned $\sim$ 0.5 mm from the HOPG surface during deposition. Focusing and space charge effects might be expected to result in cluster spot profiles that vary somewhat with deposition energy. Thus, to compare Pt XPS intensities for different samples, it was necessary to profile each cluster spot, correcting the XPS intensities for variations in the fraction of the total Pt present in the XPS analysis area.²¹ See Figure S3 and associated text.

Figure 1A shows typical spot-profile-corrected Pt 4f XP spectra recorded for samples prepared by impacting Pt₇⁺ at different energies on an HOPG sample, corrected for the energy dependence of the cluster spot profile as described in the SI. The corrected spectra are compared to the raw, uncorrected spectra in Figure S4. The XP spectral intensities are proportional to the amount of Pt present in the XPS-visible top few nanometers of the samples, weighted by the photoelectron escape probabilities. The trajectory simulations below find that even at the highest energies studied, all Pt remains within the top $\sim$ 1 nm of the sample (top 3 graphene layers). The Pt 4f photoelectron effective attenuation length (EAL), calculated using the NIST database program of Powell and Jablonski²² is $\sim$ 3.4 nm, thus the escape probability varies from 100% on the surface to $\sim$ 75% for Pt 1 nm deep. Because the Pt depth distributions are not well-enough known, we did not attempt to correct for the Pt depth distribution, but note that because depth tends to increase with energy, such a correction would tend to increase the Pt intensity at high energies, particularly at 30 eV/atom.

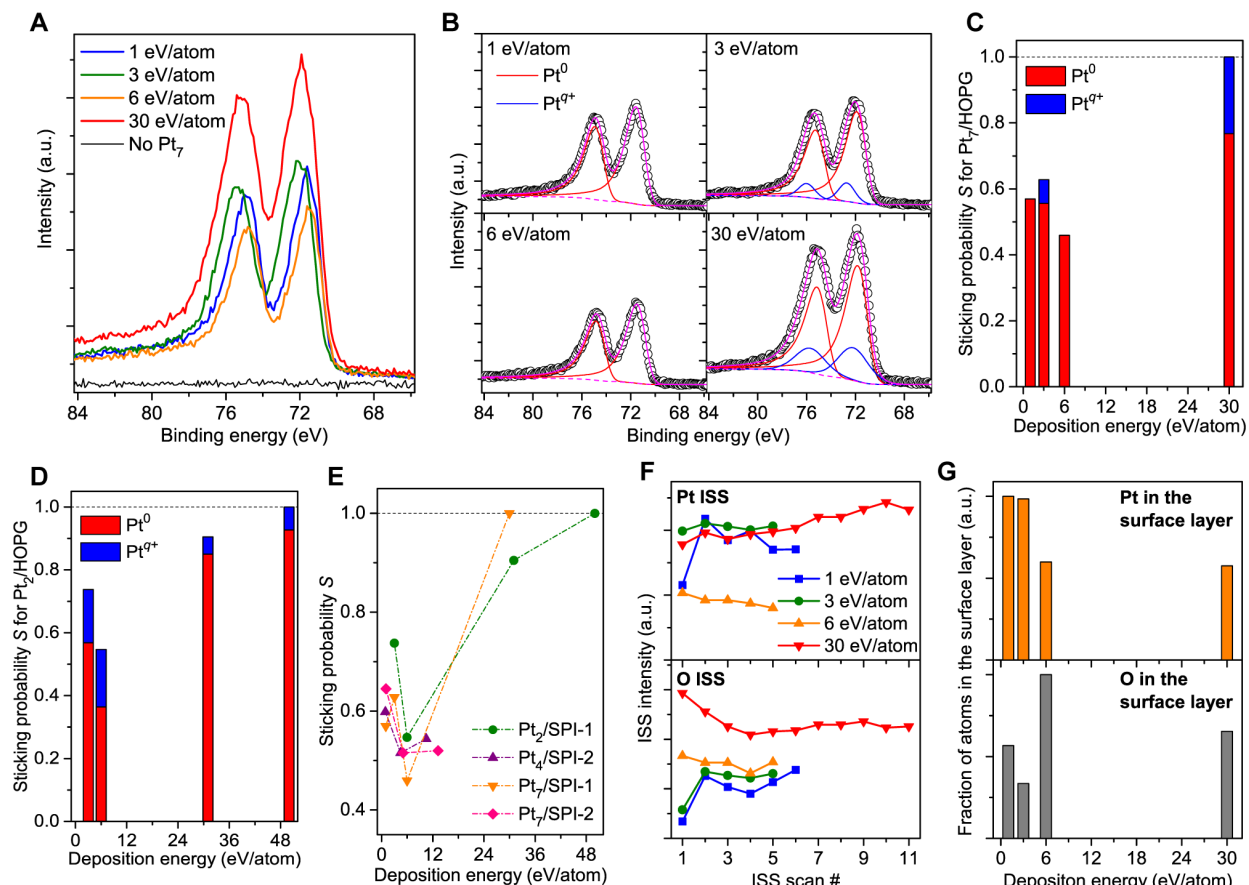


Figure 1. (A) Pt 4f XPS for 0.1 ML Pt₇/HOPG at different deposition energies, corrected for cluster spot profile. (B) Peak fitting used to integrate the Pt 4f XP spectra, showing Shirley backgrounds as dashed curves lines. (C) Pt sticking probability (S) in Pt₇ deposition at different energies, assuming $S = 1$ in the high energy limit. The red and blue bar segments represent Pt⁰ and Pt^{q+} components from the fitting results. (D) Pt sticking probability (S) in Pt₂ deposition at different energies, assuming $S = 1$ in the high energy limit. (E) Pt sticking probability (S) in other clusters. (F) Pt and O ISS intensities as a function of ISS scan number for 0.1 ML Pt₇/HOPG at different deposition energies, intensity corrected as with the XPS. (G) Relative fraction of surface layer Pt and O atoms from Pt₇ deposited at different energies estimated from Pt ISS/Pt XPS and O ISS/O XPS, respectively.

For all Pt₇ samples, the fits to the spectra in Figure 1B were dominated by a main component with 4f_{7/2} binding energy close to the 71.2 eV reference value for Pt⁽⁰⁾ in bulk Pt.²³ For 3 eV/atom, the fit improved slightly if a small component peaking just above 72 eV (4f_{7/2}) was added, and for 30 eV/atom, the contribution of this ~72 eV fit component increased. 72 eV is well below the 74.0 and 74.9 eV average binding energies reported for Pt⁽²⁺⁾ and Pt⁽⁴⁺⁾ in bulk oxides,²³ i.e., nothing resembling a true Pt oxide formed when the samples were air exposed prior to XPS analysis. Pt_n/silica samples prepared in UHV and studied by XPS before and after controlled O₂ exposure in the UHV system also showed no true oxide formation, but He⁺ ion scattering (ISS)

showed that oxygen clearly did adsorb on Pt, presumably as O adatoms.¹⁷ Several factors besides oxygen adsorption might contribute to the observed broadening toward higher binding energies for the 30 eV/atom sample. Both Pt₇ fragmentation and HOPG defect creation might be expected, and both would tend to increase Pt 4f binding energies due to decreased final relaxation in smaller Pt fragments, and Pt oxidation by Pt-C covalent bonding, respectively. These effects are explored by theory below.

Similar data were obtained for Pt₂⁺ deposited at 3, 6, 31, and 50 eV atom (Figure S5). Higher energy/atom values were used for Pt₂ in light of previous results showing that subplantation tends to require higher energies/atom for smaller clusters.²⁴

Because the total amount of Pt impinging on the HOPG surface was identical in all samples, the integrated XPS intensities should be proportional to the fraction of the Pt (delivered as Pt_n⁺) that remained bound to the HOPG, i.e., to the sticking probabilities (*S*) at each energy. These are shown for Pt₇ and Pt₂, respectively, in Figures 1C and 1D, with color indicating the contributions from the two XPS fit components. The *S* values were put on an absolute scale by assuming *S* = 1 at the highest deposition energies, as found in the trajectory studies, resulting from metal subplantation and carbon defect creation, resulting in stronger metal-carbon bonding. Figure 1E shows that *S* was not significantly different for deposition on SPI-2 grade HOPG (higher defect/step density), as might be expected because basal plane sites still dominate the surface.

S was clearly less than 1 at the lowest deposition energies, and even lower *S* values were observed at 6 eV/atom for both Pt₇ and Pt₂. The energy dependence of the Pt_n⁺ sticking is qualitatively similar to that measured in greater detail by Yamaguchi *et al.* for Ag_n⁺ impacts on HOPG.¹¹ They also observed moderately high sticking probabilities for all cluster sizes at their lowest deposition energies, decreasing at intermediate energies, then increasing to higher and near-constant values at high energies. The main difference was that the decrease at intermediate energies was larger for Ag_n⁺ compared to Pt₂⁺ and Pt₇⁺. More efficient sticking for Pt is unsurprising because the higher Pt/C mass ratio implies that energetic Pt clusters are less likely to backscatter, and more likely to penetrate the surface, compared to Ag clusters.

ISS was also used to probe as-deposited Pt_n/HOPG samples produced at different deposition energies. Figure S6 shows the raw spectra from a series of ISS scans taken on Pt₇/HOPG samples deposited at 1, 3, 6, and 30 eV/atom. ISS peaks result from scattering of He⁺ ions from single atoms, mostly in the topmost surface layer, while multiple and sub-surface

scattering events primarily contribute to a broad background, which tends to rise toward low E/E_0 ($E_0 = 1$ keV).²⁵ The approach to subtracting this background contribution is shown in Figure S7.

Thus, the Pt and O ISS peak intensities are proportional to the *numbers* of Pt and O atoms present in the topmost sample layer. For Pt, this depends both on the Pt_n sticking probability and on probability that the Pt is either subplanted below the surface layer or covered by adsorbates that block He^+ scattering. Figure 1F plots the Pt and O ISS intensities for the four Pt_7 samples, and how they changed during the series of ISS scans run on each sample.

Note that for the 1 eV/atom sample, the initial Pt ISS intensity was quite low, increased substantially in the 2nd ISS scan, then decreased slowly thereafter. This is typical behavior for clusters with initial coverage of weakly-bound adsorbates,²⁶ as would be expected for the air-exposed sample. Because 1 keV He^+ sputters such adsorbates more rapidly than underlying Pt atoms, it is possible to sputter off most of the adsorbate while most of the Pt remains on the surface, resulting in the observed rapid initial increase in the Pt ISS intensity. Once the adsorbates were removed, the much slower Pt sputtering would cause the slowly decreasing Pt ISS signal.

The obvious question is why the rapid initial increase was not seen for the other samples, even though they all were air exposed. This simply reflects the fact that all four ~ 2 mm cluster spots were deposited on a single 10 x 10 mm HOPG substrate, separated by only a few millimeters. The He^+ ISS beam was focused to ~ 3 mm diameter but had a low intensity halo extending to ~ 5 mm diameter. Thus, during the 8 ISS runs done for the 1 eV/atom spot, which was analyzed first, the neighboring spots also received some He^+ exposure – evidently sufficient to remove the weakly bound adsorbates prior to analysis of those spots. For this reason, the “initial” Pt ISS intensities were approximated by the intensities recorded in the 2nd scan on each sample.

Since XPS intensities are proportional to sticking probabilities, the ISS/XPS ratio is proportional to the *fraction* of Pt present that is exposed in surface sites, and the initial fraction for each sample is presented in Figure 1G, again based on the 2nd ISS scans. Note that neither the numbers nor the fractions of surface Pt atoms can be put on an absolute basis directly from the ISS intensities, however, it is not unreasonable to expect that for low deposition energies, where subplantation is energetically impossible, all Pt present should be on the surface, and therefore the surface Pt fraction should be $\sim 100\%$ at low deposition energies.

This conclusion is consistent with the observation that for both the 1 eV/atom and 3 eV/atom spots, the “initial” ISS intensities were high and quite similar because all the Pt would

have been on the surface, and both slowly decreased over the series of scans as Pt slowly sputtered away. The initial Pt ISS intensity for the 30 eV/atom spot was similar to those for the 1 and 3 eV/atom spots but slowly *increased* over the series of ISS runs. As shown in Figure 1C, the sticking probability at 30 eV/atom was substantially higher than those at lower energies, but the fraction of Pt present in the surface layer (Figure 1G) was substantially smaller compared to the 1 or 3 eV/atom samples. Thus, the 30 eV/atom spot had a similar amount of surface Pt, but also a substantial subplanted amount. The slow increase in Pt intensity over the series of ISS scans indicates that carbon sputtering exposed initially subplanted Pt faster than Pt sputtering removed Pt from the surface. Thus, the ISS and XPS results show that sticking is efficient at high energies, but with substantial subplantation. This potentially would pin the clusters at the impact sites, but presumably also reduce their electrochemical activity because only a fraction of the Pt is on the surface.

Therefore, the 6 eV/atom sample was of particular interest, as the total energy (42 eV/cluster) is sufficient to break multiple C-C bonds, possibly pinning the clusters at their impact sites, but we might expect less Pt subplantation than at 30 eV/atom. Figure 1F shows that the initial number of surface Pt atoms was the lowest of any sample, partly because the sticking probability was low (Figure 1C), but Figure 1G shows that substantial subplantation occurred at 6 eV/atom. The decrease in Pt intensity with ISS scan number for 6 eV/atom indicates that exposure of subplanted or adsorbate-covered Pt atoms was insufficient to offset the sputter loss of Pt from the surface for this deposition energy.

The lower frame of Figure 1F shows how the O ISS intensities varied with Pt₇ deposition energy and ISS scan number. As with the Pt results, we focus on the 2nd and later scans. The O ISS signals result from O₂ adsorption when the UHV-prepared samples were exposed to air for transfer to the spectrometer, with adsorption energy high enough that the oxygen remained bound when the samples were reintroduced to UHV for XPS and ISS analysis ($E_{\text{desorption}} \geq \sim 1$ eV). O₂ physisorption at undamaged HOPG basal plane sites would be far too weak, but chemisorption at both exposed Pt sites and impact-created carbon defects could bind O strongly enough. The result, that O ISS signal increased monotonically with increasing deposition energy, is consistent with this expectation. At 1 eV/atom and 3 eV/atom, permanent C-C bond scission and defect creation is not expected (see simulations below), thus, oxygen binding is limited to Pt sites, and the sticking probabilities are relatively low at low energies (Figure 1C). At 6 eV/atom, the number of surface

Pt atoms (Figure 1F) is small, but the energy is high enough for carbon defect creation, providing additional O binding sites, and the high O ISS signal for 30 eV/atom reflects both relatively high surface Pt numbers (Figure 1F) and likely creation of more carbon defects capable of binding additional oxygen.²⁷

Imaging studies were carried out by a variety of electron microscopy methods for samples prepared by energetic cluster deposition on multilayer graphene TEM grids from several vendors. Selected images are shown in Figure S8 and discussed in the SI, along with issues associated with grid contamination. In essence, clusters were observed with atomic resolution, but with evidence of both cluster shattering and sintering. The fact that shattering to isolated atoms was observed even for samples prepared with deposition energies far too low to drive shattering, suggests that beam effects were severe.

DFT-simulations of ballistic deposition of Pt_n clusters

Born-Oppenheimer Molecular Dynamics (BOMD) simulations were used to model the impacts of Pt_n ($n = 2-4$) clusters on the HOPG surface. A detailed description of the simulation protocol is provided in the SI. For each deposition energy, enough trajectories were simulated with differences in initial cluster orientation and impact site, to capture the range of possible outcomes with semi-quantitative statistics.

For all cluster sizes, simulations were performed at 2, 10, 20, 40, 60, 80, and 100 eV kinetic energy *per cluster*; for Pt₄, an additional 120 eV case was considered. The *per atom* energies referenced above are simply the *per cluster* values, divided by the cluster size. Reflecting the increase in complexity with cluster size, for each energy 75 trajectories were sampled for Pt₂, 90 for Pt₃, and 105 for Pt₄, ensuring a statistically meaningful ensemble for each case. The initial orientation of the cluster relative to the HOPG surface was sampled by rotating the cluster around its center of mass (COM). Additionally, for each cluster size, the initial configurations were evenly divided into three groups based on the COM impact position: directly above a carbon atom in the top monolayer of HOPG, above the center of a C-C bond, and above the center of a C₆ ring. Note that the trajectory outcomes were only weakly dependent on the COM impact position.

Instead, the initial kinetic energy of the incoming cluster plays a dominant role in shaping the outcome, influencing surface interaction strength, penetration depth, defect formation, sticking, and cluster fragmentation. Broadly, the observed outcomes can be classified into three categories: (1) the cluster scatters from the HOPG surface, (2) the cluster adsorbs on the surface

with no C-C or Pt-Pt bond scission or covalent Pt-C bond formation, (3) the impact drives implantation into the surface, with Pt-Pt and C-C bond scission, forming a variety carbon defects and bonded Pt-C species, leading to immobilization. We begin by examining the energy-dependent behavior of Pt_2 to establish a baseline for interpreting the more complex dynamics for larger clusters. Note that the figures below show only the most typical structures observed under different deposition conditions.

In the energy range from 2 to 20 eV, i.e., up to 10 eV/atom, Pt_2 clusters predominantly scattered from or adsorbed on the HOPG, without dissociating or damaging the surface. Scattering dominated in this energy range. For example, at 2 eV (1 eV/atom), out of 75 simulated trajectories, 65% (49 cases) resulted in scattering, i.e., clusters bounced off the surface without adhering. The other 35% resulted in adsorption, either directly (16 cases), or by a re-adsorption process in which clusters initially bounced but were re-captured and adsorbed on the surface within the 2.5 ps simulation time (10 cases). The adsorbed clusters were mostly bound to carbon atoms or to the

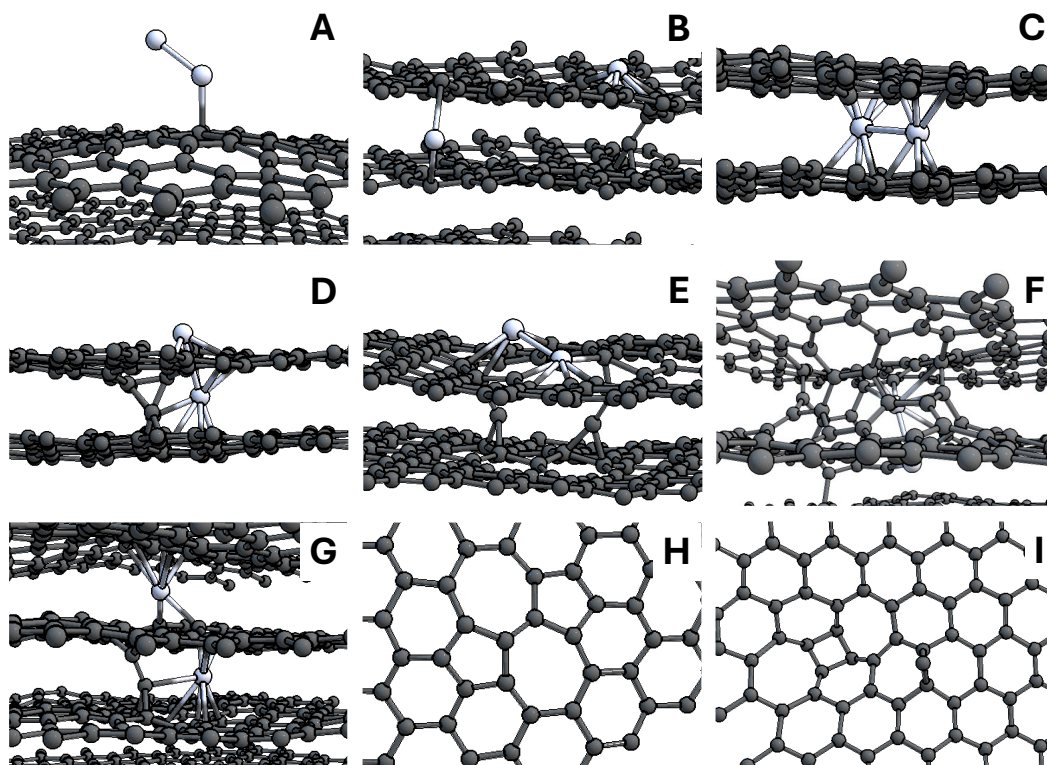


Figure 2. Main structural patterns arising from chemical immobilization of Pt_2 upon initial kinetic energy of 40-60 eV per cluster: medium-energy regime.

hexagonal ring centers, predominantly in vertical orientation (23 cases, Figure 2A), with horizontal binding being relatively rare (3 cases). Thus, even at low kinetic energies, Pt₂ clusters tend to adsorb into energetically favorable configurations, influenced by both orientation and local surface site, with sticking probability significantly below unity, consistent with the XPS measurements. Given the uncertainties and approximations in the simulations, including relatively limited statistics, the results should be interpreted as qualitative rather than quantitative. Compiled statistics across all energies and cluster sizes are presented in Table 1.

At 10 eV, i.e., 5 eV/atom, scattering occurred in 52% (39 cases) of trajectories, with the balance adsorbing. Direct adsorption occurred in only 3 trajectories (4%), as might be expected given the need to dissipate more energy to allow sticking, however, re-adsorption occurred in 33 trajectories (44%), i.e., re-adsorption was more efficient at 10 eV, than at 2 eV. The final adsorption configurations again displayed a strong preference for vertical alignment (all 36 cases), with clusters anchoring predominantly near carbon atoms (64%), and to a lesser extent near hexagon centers or C-C bond midpoints (36%). We attribute the slightly increased adsorption

Table 1: Percentages of the typical outcomes of the cluster deposition as a function of the kinetic energy. Pt-Pt bond breaking may lead either to scatter or to deposition, or to both.

	2 eV			10 eV			20 eV		
	scatter	deposition	Pt-Pt bond breaking	scatter	deposition	Pt-Pt bond breaking	scatter	deposition	Pt-Pt bo breakir
Pt ₂	65	35	0	52	48	0	55	45	0
Pt ₃	59	41	0	29	71	0	59	41	0
Pt ₄	51	49	0	35	65	0	47	53	0
	40 eV			60 eV			80 eV		
	scatter	deposition	Pt-Pt bond breaking	scatter	deposition	Pt-Pt bond breaking	scatter	deposition	Pt-Pt bo breaking
Pt ₂	12	88	23	5	95	32	0	100	52
Pt ₃	32	68	22	11	89	33	7	93	23
Pt ₄	37	63	0	47	53	9	22	78	29
	100 eV			120 eV					
	scatter	deposition	Pt-Pt bond breaking	scatter	deposition	Pt-Pt bond breaking			
Pt ₂	0	100	39	n/a					
Pt ₃	0	100	46						
Pt ₄	12	88	26						
	0	100	48	0	100	48			

probability at 10 eV to enhanced energy dissipation during impact, potentially facilitated by transient, non-permanent rearrangements of C-C bonds in the graphene lattice. Similar behavior was observed at a kinetic energy of 20 eV (10 eV/atom), where 55% of all trajectories (41 cases) resulted in scattering, while the remaining 34 cases involved re-adsorption; no instances of direct adsorption were recorded. The final configurations continued to favor a vertical orientation of the Pt₂ cluster, with anchoring site preferences like those observed at 10 eV.

At 40 eV (20 eV/atom), a significant transition in deposition behavior was observed. Only 12% of trajectories (9 cases) scattered without substantial interaction, while 88% resulted in penetration of the first graphene layer. Pt-Pt bond cleavage occurred in 23% of the penetration events (15 cases), mostly in impacts with initially vertical cluster orientations (Figure 2B), which enable deeper penetration due to concentrated energy transfer at the impact site. Impacts in more horizontal cluster orientations tended to result in both Pt atoms becoming trapped between the first and second HOPG layers (Figure 2C), typically preserving the Pt-Pt bond. 57% of all trajectories (43 cases) resulted in at least one Pt atom being located within or above the first graphene layer, i.e., surface accessible. Of these, 33 cases (44% of total trajectories) had one accessible Pt atom (Figures 2D), while 10 cases (13%) had both atoms accessible. Dual-atom accessibility typically was associated with larger or more complex structural defects in the HOPG surface (Figure 2E).

At 60 eV (30 eV/atom), the trends observed at 40 eV became more pronounced, with only 5% of trajectories resulting in scattering (i.e., $S = 0.95$), with penetration as the dominant outcome (95%, 71 cases). Pt-Pt bond dissociation increased to 32% (24 cases), frequently associated with defect formation and the development of interlayer composites (Figure 2D, 2F-G). Pt surface accessibility was observed in 41% of trajectories (31 cases), primarily involving single Pt atoms stabilized by hole defects in the first graphene layer. Dual-atom accessibility remained relatively rare (8%, 6 cases). The decline in Pt surface accessibility at this and higher energies is attributed to deeper cluster penetration – into the first or second HOPG layers – effectively burying the Pt atoms beneath the surface (Figures 2F, G), consistent with the ISS results.

At 80 eV (40 eV/atom), penetration occurred in all trajectories ($S = 1$), and Pt-Pt bond dissociation increased to 52% (39 cases). More extensive defect structures appeared, including C5-C8 ring defects (Figure 2H) and biphenylene-like ring rearrangements (Figure 2I), while interlayer bonding motifs evolved beyond those observed at lower energies. The penetration depth extended

to between one and three HOPG layers. Surface-accessible Pt was found in 28% of all trajectories (17 cases), in most cases with only a single Pt atom on the surface (13 cases).

100 eV (50 eV/atom) also resulted in 100% penetrating trajectories, and Pt surface accessibility continued to decline. Massive defect formation spanning one to three HOPG layers was found in 79% of cases (59 trajectories), while Pt-Pt bond dissociation occurred in 39% (29 cases). Only 9% of trajectories (7 cases) resulted in surface accessible Pt, in all cases involving only a single Pt atom.

In summary, in the 2–20 eV kinetic energy range (i.e., 1–10 eV/atom), Pt₂ clusters interacted with the HOPG surface primarily through intact adsorption or scattering, and no Pt-Pt or C-C bond scission was observed. At 40 eV (20 eV/atom) and above, the clusters increasingly penetrated into the HOPG, with both C-C and Pt-Pt bond disruption, leading to Pt-C chemical interactions, HOPG structural transformations, and carbon defect formation. The highest fraction of trajectories leading to Pt available on the surface was observed at 40 eV (20 eV/atom), where 57% of trajectories produced configurations with at least one surface-accessible Pt atom. At higher energies, the Pt sticking probability was 1.0, however, the Pt surface accessibility declined due to deeper penetration and more extensive lattice disruption.

Similar behavior was observed in trajectories for Pt₃ and Pt₄ clusters, although the onset of Pt-Pt and C-C bond scission and Pt-C bond formation occurred at higher *per* cluster kinetic energies, but lower *per* atom energies. For instance, Pt₃ clusters remained largely inert in the 2–20 eV range, where non-reactive scattering and re-adsorption dominate, often producing vertically oriented adsorbates with a single Pt-C contact (Figure 3A) and no disruption to the HOPG lattice. Reactions first appeared in trajectories near 40 eV (~13 eV/atom), with occasional C-C bond scission and only 4% of trajectories forming surface-accessible Pt₂ fragments trapped at defects (Figure 3B). Pt₃ impacts at 60 eV (20 eV/atom) led to deep penetration and interlayer composite formation, however, only 29% of trajectories left any Pt atoms accessible on the surface, mostly involving partial burial or asymmetric exposure (Figures 3B–D). At 80 eV, 63% of Pt₃ trajectories left at least one Pt atom near the surface, but this fraction declined again at 100 eV, where fragmentation and deep embedding reduced surface accessibility to 43% (Figure 3E).

For Pt₄, similar trends were observed, but the onset of bond scission, formation, and penetration occurred at even higher *per* cluster energies, although the *per* atom energies were similar. Most impacts in the 2–40 eV/cluster range resulted either in scattering or sticking via re-

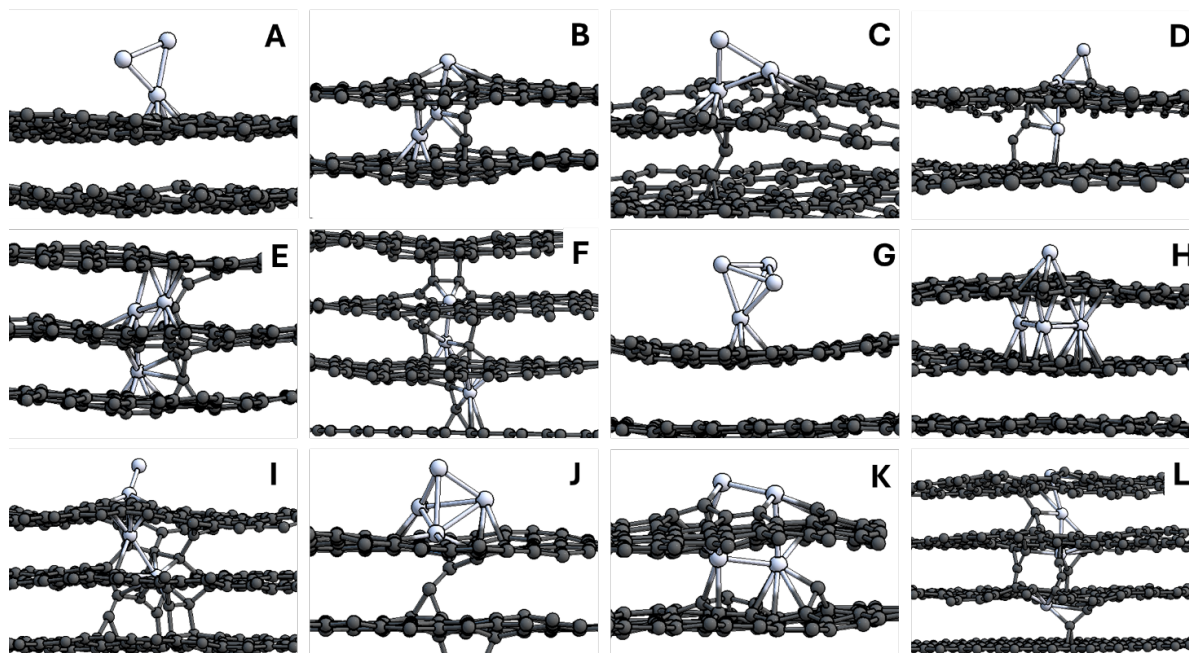


Figure 3. Main structural patterns arising from chemical immobilization of Pt₃ (A-E) and Pt₄ (F-I)

adsorption, without lasting structural change (Figure 3G). At 60 eV (15 eV/atom), shallow penetration and temporary lattice rearrangements were observed but these typically relaxed within the simulation timeframe. Persistent bond scission and Pt-C bond formation first appeared at 80 eV (20 eV/atom), with 47% of trajectories resulting in at least one Pt atom accessible on the surface (Figures 3H) and 12% with multi-atom accessibility (Figures 3I-K). The structures were often stabilized by interlayer C-C bonding, hole-type defects, and composite Pt-C frameworks spanning multiple graphene layers (Figures 3L). At higher energies, surface accessibility decreased (less than 38%) due to deeper penetration (1-3 layers) and extensive lattice disruption.

Summary of the dynamics of energetic cluster deposition.

XPS and ISS (Figure 1) are generally in good agreement with the BOMD results. Both experiments and trajectories observed efficient sticking and subplantation at high impact energies, and the trajectories suggest that the absolute sticking probability should be 1.0 in the high energy limit, as expected from kinematics. In the experiments, the sticking probabilities at the lowest energies were 30 to 40% lower than at the highest energies, consistent with the trajectory finding of substantial scattering even for energies as low as 1 eV/atom.

The only real discrepancy is that the trajectories found that sticking probabilities increased monotonically as the impact energy increased, whereas XPS showed that the sticking probability went through a minimum at intermediate energies, before increasing to the high energy limit.

Murakami and co-workers also observed a pronounced minimum in sticking for Ag_n^+ -HOPG collisions at intermediate energies.¹¹ The origin of the sticking minima observed experimentally is unclear, however, given the weak bonding of Pt_n with intact HOPG sites (e.g. Pt_4 is calculated to have $E_{\text{adsorption}} \approx 3$ eV on intact HOPG), one possible explanation is that cluster impacts might drive desorption of (i.e., sputter) Pt_n already present on the surface. This effect would presumably increase with increasing impact energy, but only up to the point where carbon defect creation and subplantation drastically increase the Pt-carbon binding strength. Thus sputtering by cluster impacts may account for the observation that S initially drops with increasing energy, before increasing at high energies. Such secondary effects of cluster impacts are not feasible for BOMD simulation.

Electrochemical Measurements

We measured cyclic voltammograms (CVs) for HER in 0.1 M HClO_4 at Pt/HOPG electrodes prepared by 0.1 ML deposition of Pt_n^+ at different energies. These measurements probe the activity of the structures produced by variable energy Pt_n deposition, and also provide insight regarding the amount Pt accessible on the electrode surfaces, as opposed to Pt subplanted below the surface or failing to stick during deposition.

Figures 4A-C show typical voltammetric responses on 0.1 ML Pt_n /HOPG electrodes prepared with various Pt_n^+ deposited at different energies. For readability, only the negative-going sweeps are shown, but the full CVs are given in Fig S9. The data in Figure 4, and in all other experimental figures below, have been background subtracted as illustrated in Figure S10 A-C, and corrected for small resistive effects on the potentials, as illustrated in Figure S11.

The currents in Figure 4 are taken from the 4th to 6th CV cycle for each sample, just after the CVs for the air-exposed samples had stabilized, and once stabilized, the activity was stable in repeated CVs over this potential range. The electrochemical characterization focused primarily on low and intermediate deposition energies, where substantial Pt was left on the surface (Figure 1F), consistent with the trajectory simulations. Only a few HER experiments were done with clusters deposited at high energies (e.g. Pt_2 at 50 eV/atom) where substantial subplantation is observed in the trajectories and ISS. Additional high-deposition-energy examples are discussed below. The currents in Figure 4 have not been normalized to the Pt XPS intensities, i.e., they are not corrected for the energy or cluster size dependence of the sticking probability. For comparison, analogous data for samples prepared by soft-landing of Pt_4 and Pt_7 on FTO electrodes are also shown.

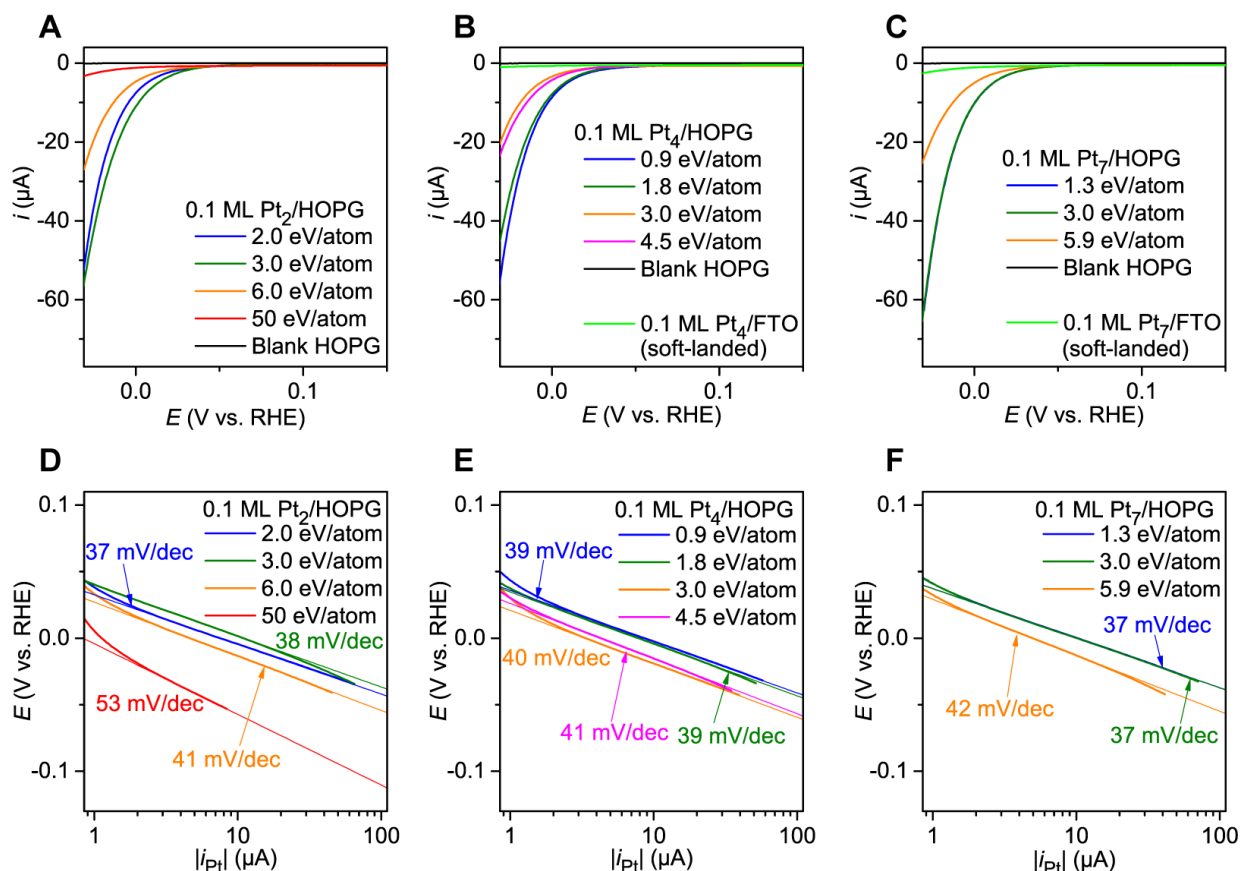


Figure 4. A-C: Voltammetric curves in 0.1 M HClO_4 for 0.1 ML of Pt_2 , Pt_4 , and Pt_7 deposited on HOPG at various deposition energies. Blank HOPG refers to a background response (i_{HOPG}) from a Pt-free HOPG electrode. i_{Pt} is a background-subtracted current, namely, $i_{\text{Pt}} = i - 0.9i_{\text{HOPG}}$. Data for Pt_4 and Pt_7 soft landed on FTO are shown for comparison. D-F: Tafel plots derived from the data in A-C.

Several points are clear. The HER currents for all the Pt_n /HOPG samples are large compared to those for Pt_n /FTO, even though the XPS and trajectory results show that the Pt_n -HOPG sticking probabilities would have been below unity for most of these samples. The currents for Pt_2 , Pt_4 , and Pt_7 clusters deposited at low energies are large, essentially independent of the deposited cluster size, and only weakly dependent on the deposition energy. Under these conditions, the sticking probabilities are relatively high (60 to 70%), and the available energy is too low to drive defect creation or to subplant Pt atoms. Thus, these clusters would have been weakly bound to the intact HOPG support, raising the possibility that the deposited size may not have been preserved due to diffusion and agglomeration.

For higher deposition energies, the currents are lower and depend on both the deposition energy and cluster size. For the highest energies, such as Pt₂ at 50 eV/atom and other examples presented below, the activity is quite small, despite XPS and trajectory simulations indicating high sticking probability. Low activity is, however, consistent with Pt subplantation at high energies, leaving little surface-accessible Pt. At intermediate energies (e.g. 6 eV/atom for both Pt₂ and Pt₇), XPS shows that the sticking probabilities are reduced compared to low energies, and at least for Pt₇, the energy is high enough to result in significant subplantation, further reducing the amount of Pt on the surface (Figure 1F), accessible to electrolyte.

Tafel plots derived from the currents in A-C are shown in D-F. The Tafel slopes derived from the tangent lines are mostly in the range between 37 and 42 mV/decade, with a general trend toward higher Tafel slope for higher deposition energy. Indeed, the only value outside this range is 53 mV/decade observed for Pt₂/HOPG deposited at 50 eV/atom, where both ISS and trajectories suggest that much of the Pt is subplanted below the surface. It is worth noting that a Tafel slope of 40 mV/dec is often associated with the Volmer–Heyrovsky mechanism for the HER kinetics in acidic media,¹ i.e., with rate limited by a Heyrovsky step (see below).

We can approximately correct for the effects of sticking probability by normalizing the HER currents to the XPS intensities, as illustrated in Figure S10 D-E, and that does reduce the dependence of the HER activity on deposition energy, as shown in Figure 5A and B. Even with this correction, however, the activities at 5.9 eV/atom for Pt₇ and at 50 eV/atom for Pt₂ are smaller than those observed at lower energies, presumably because not all the Pt is in the electrolyte-exposed surface layer. The currents can be normalized to the amount of Pt in the surface layer using ISS data (Figure 1F), as illustrated in Figure S10 F-H. The result

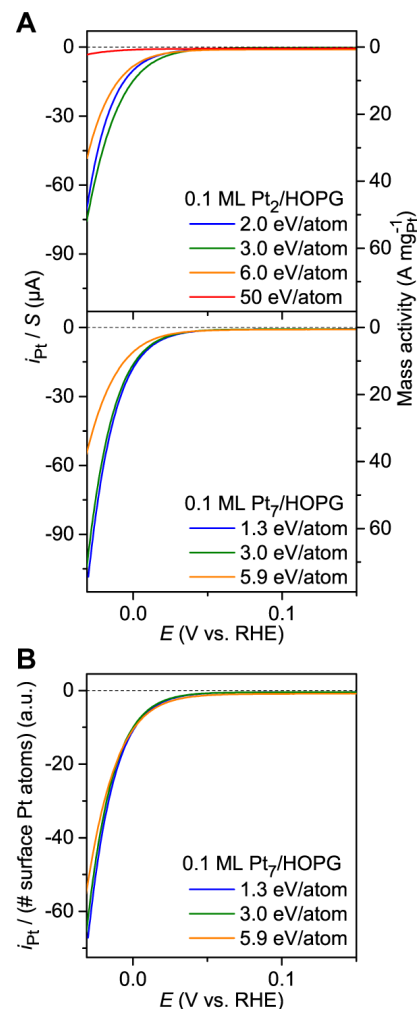


Figure 5 (A) HER activities for Pt₂/HOPG and Pt₇/HOPG normalized to XPS intensities. (B) HER activities for Pt₇/HOPG normalized to ISS intensities.

for the Pt₇/HOPG samples is shown in Figure 5C, and it appears that ISS normalization slightly over-corrects for the effects of Pt subplantation at ~5.9 eV/atom. The effects of CV cycling on electrodes with subplanted Pt are discussed below.

HER activity modeling

Based on the trajectories presented above for energetic impact of Pt₂, Pt₃ and Pt₄ clusters, four representative structures were chosen for HER analysis for each deposited cluster size. These are shown in Figure 6 and designated as Pt_n_m, where n is the deposited cluster size and m is an index for the four structures studied for each Pt_n size. Because the goal was to examine the activity as HER catalysts under conditions where pinning at defects might be expected to stabilize the clusters against sintering, the structures chosen each have C-C bonds broken with Pt-C bonds formed, and each has at least one Pt atom exposed on the surface. The structures are, thus, characteristic of intermediate deposition energies, rather than soft-landing (where sintering to larger clusters is likely) or the highest deposition energies, where deeper implantation dominates.

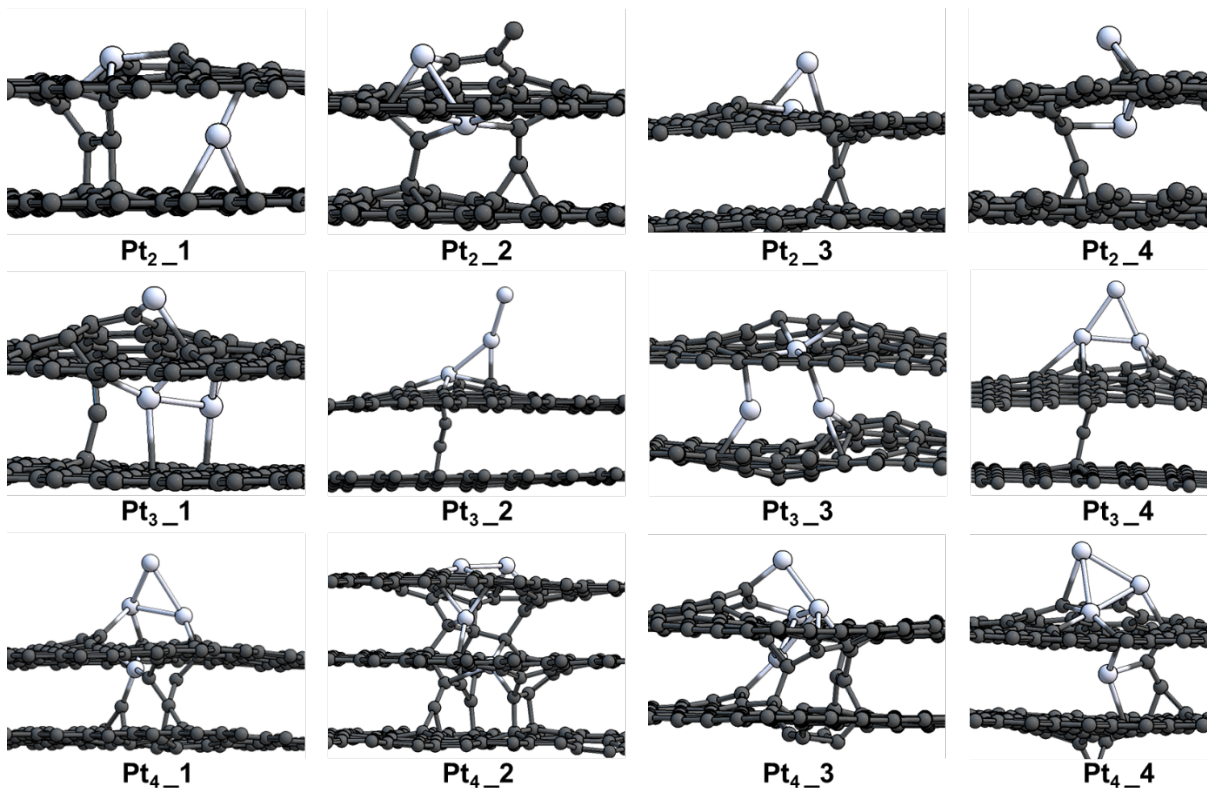


Figure 6. Structures selected for the HER activity study. Pt_n_m, where n (2–4) indicates the number of Pt atoms in the cluster, and m (1–4) denotes the index of the representative structure selected for each cluster size.

For each of the 12 Pt_n_m structures, we computed the hydrogen coverage distributions under experimental conditions (pH = 1), by sequentially adding hydrogen atoms to each structure until the adsorption free energy of the next hydrogen became positive. Calculations were based on the computational hydrogen electrode (CHE) model,²⁸ in which the chemical potential of a proton–electron pair (H⁺ + e[−]) is referenced to that of ½ H₂ gas under standard conditions. We then calculated the room temperature Boltzmann distribution of the H-covered structures based on the calculated H adsorption energies. Here, we assumed that the structures of the clusters themselves were kinetically controlled (i.e., determined by the deposition dynamics) and their intrinsic energies do not follow thermodynamic equilibrium. The Boltzmann populations of H coverage for each isomer are plotted in Figure S12, with each surface-exposed Pt atom binding up to 2 H atoms, with H bound in atop, Pt-Pt bridging sites, and Pt-C bridging sites, as well as to C surface defects.

To estimate the HER activity of each of the H-covered Pt_n_m structures, we evaluated the activation energies for both Volmer-Heyrovsky (V-H) and Volmer-Tafel (V-T) mechanistic pathways,^{5, 29} where “n•H*” designates n H atoms bound to one of the Pt_n_m structures:

- **Volmer–Heyrovsky pathway**
 - Volmer: n•H* + H⁺ + e[−] → (n+1)•H*
 - Heyrovsky: (n+1)•H* + H⁺ + e[−] → n•H* + H₂
- **Volmer–Tafel pathway**
 - Volmer 1: n•H* + H⁺ + e[−] → (n+1)•H*
 - Volmer 2: (n+1)•H* + H⁺ + e[−] → (n+2)•H*
 - Tafel: (n+2)•H* → n•H* + H₂

For each H-covered Pt_n_m structure with significant Boltzmann population, the free energy change for both V-H and V-T pathways was calculated, and the results are shown in Figure 7A. The free energy barrier for the rate-determining step (ΔG_{rds}) is taken as the largest positive free energy change along a given reaction pathway and is assumed to be a thermodynamic descriptor of catalytic activity, with lower values indicating more favorable reaction pathways. As shown in Figure 7A, the ΔG_{rds} values for the Heyrovsky pathway were lower than those for the Tafel pathway for almost all structures and H coverages, suggesting that the Volmer–Heyrovsky mechanism is the dominant HER pathway on these Pt clusters. That conclusion is consistent with the measured Tafel slopes (Figure 4D-F).

Next, the ΔG_{rds} values for each $\text{Pt}_n\text{-m}$ were averaged over the Boltzmann hydrogen coverage populations (Figure S12) to estimate the reactivity for each $\text{Pt}_n\text{-m}$ structure. This analysis yielded average ΔG_{rds} ranging from 0.06 to 0.22 eV for the different cluster sizes and isomers (red squares in Figure 7A). In the experiments, the activity is additionally averaged over the

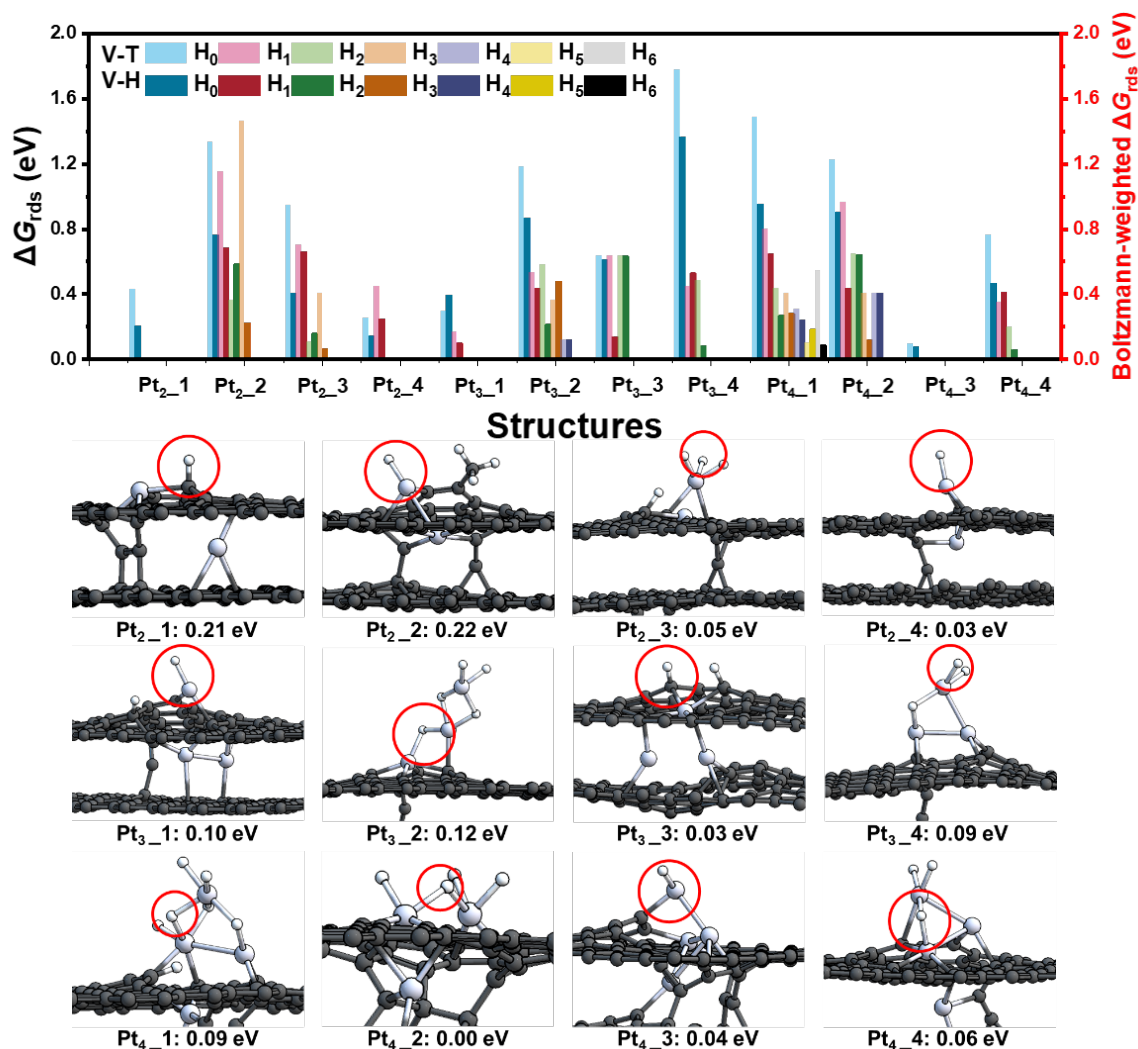


Figure 7. (A) ΔG_{rds} of Volume-Tafel (V-T) and Volume-Heyrovsky (V-H) mechanism of HER, on different Pt clusters with various hydrogenation states. The red line indicates the Boltzmann-weighted ΔG_{rds} for each structure. (B) Representative structures of Pt clusters that contribute most significantly to the HER activity for each structure. Red circles indicate the most active HER active sites under each hydrogen coverage, where "Pt" and "Pt-coordinated C" denote whether the reaction site is a Pt atom or a C atom coordinated with Pt.

distributions of structures formed for each cluster size at each impact energy, but we have not attempted this averaging because the trajectory statistics are not complete enough. Nonetheless, it is clear that averaging over the Pt structures would further reduce the variation in ΔG_{rds} for different deposited cluster sizes. Given the intrinsic errors of DFT, the computational hydrogen electrode (CHE) model, and the implicit solvation model, the differences in the averaged barriers are probably not significant, i.e., DFT suggests that the HER activity should not be strongly dependent on the size of the Pt cluster deposited, consistent with the experiments.

Figure 7B shows the most reactive H-covered structure for each cluster isomer, i.e., the structures with the lowest ΔG_{rds} (shortest bars in Figure 7A). As noted, reaction is predicted to occur by a Heyrovsky step, i.e., by H^+ reaction with the H atoms circled in red. These reactive H atoms are typically bound on surface Pt atoms or on carbon atoms directly coordinated to Pt. The corresponding ΔG_{rds} for these most reactive structures lie between 0 and 0.22 eV, again suggesting that HER activity should be at most weakly size-dependent, at least for the structures formed by hard landing of Pt_2 to Pt_4 clusters.

As shown in the BOMD simulations, high deposition energy leads to Pt clusters becoming partially subplanted but also creating surface carbon defects that can bind H (Figures 6 and 7). As noted, H bound to C atoms that are bound to Pt have ΔG_{rds} values comparable to H bound to Pt, but it is also important to consider the possible contributions to HER from reaction with H atoms bound to isolated carbon defects, i.e., those not bound to Pt. For this purpose, we examined a representative structure with Pt entirely subplanted below the surface, but with carbon defects in the surface layer, as might be produced at high deposition energies. The lowest HER ΔG_{rds} for this structure was 0.56 eV, i.e., more than double the maximum ΔG_{rds} found for the reactive sites shown in Figure 7B. Thus, we infer that isolated carbon defects, without attached Pt, bind H too strongly to contribute significantly to the HER activity. An experimental test of this point is discussed below.

In summary, DFT indicates that, as expected, deposition at low energies results in Pt_n on top of the undamaged HOPG surface, which we have not attempted to model further because such weakly bound clusters almost certainly diffuse and aggregate. Intermediate deposition energies create more strongly bound structures with Pt atoms and carbon defects on the surface, often with additional Pt and C defects in the sub-surface, exemplified by the $\text{Pt}_n\text{-m}$ structures in Figure 6. The ensemble-averaged HER energetics are weakly dependent on the $\text{Pt}_n\text{-m}$ isomer, and even

more weakly dependent on deposited Pt_n size. At high deposition energies, the Pt is largely buried beneath the surface layer, and the carbon defects present on the surface are predicted to be significantly less active for HER, resulting in overall low activity, consistent with the trends observed experimentally.

Effects of potential cycling on HER activity: Stability and re-emergence of subplanted Pt.

Questions raised by the above results include whether the active structures produced by energetic Pt_n deposition are stable respect to sintering and Pt dissolution under electrochemical conditions, and whether initially subplanted Pt might emerge into electrolyte-accessible surface sites under some conditions. The results in Figure 4 are based on data from the 4th to 6th CV cycle for each sample, immediately after the currents for the air-exposed samples had stabilized. The currents remained stable for at least a few dozen additional CVs, provided that the potential scan range remained narrow, i.e., confined to potentials near the HER onset.

The effects of cycling to higher (more oxidizing) potentials were tested for electrodes prepared by 0.1 ML deposition of Pt_1 at different energies (Figure S13), and for an electrode prepared by hard-landing Pt_4 at 13 eV/atom (Figure S14). In

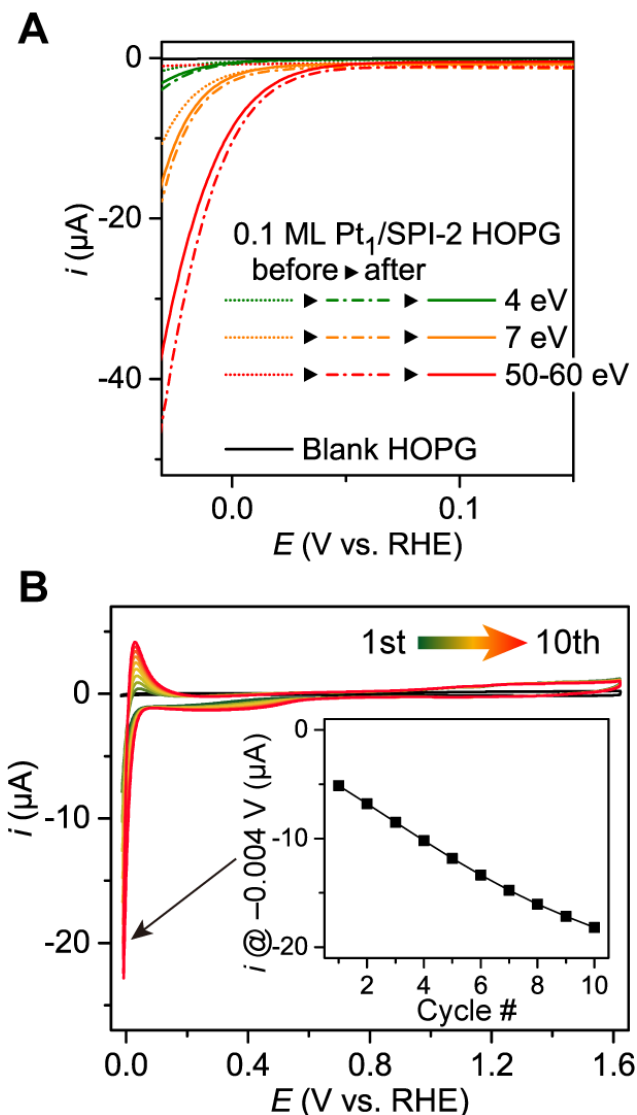


Figure 8. (A) Comparing the effects of CV cycling on HER activity for Pt_1 deposited at different energies. (B) Increase in HER current over 10 wide range CVs for Pt_1 /HOPG deposited at 50 to 60 eV.

those experiments, the HER activity of the as-prepared electrodes was first probed by a set of narrow potential range CVs, with additional narrow range CVs run to verify that the currents were stable under these conditions. Next, sets of CVs to higher upper potential limits were run, scanning the electrodes through the onsets for Pt oxidation and the oxygen evolution reaction (OER). See the SI (Figures S13 and S14) for details.

Figure 8 summarizes the experiments with Pt₁ deposited at energies of ~4 eV, ~7 eV, and between 50-60 eV. The initial HER current for each samples is shown by dotted curves in Figure 8A, the currents measured immediately following scans to higher upper potential limits are shown by dot-dash curves, and the current in a subsequent CV are shown as solid curves. For the two lower deposition energies, neither of which should have led to significant subplantation, the currents were somewhat higher immediately following scanning to oxidizing potentials, however, in subsequent narrow range CVs, the currents decreased back to roughly the initial values, i.e., the increase in activity induced by cycling to oxidizing potentials was only transient.

In contrast, for the sample prepared by Pt₁ deposition at 50 to 60 eV, i.e., with much of the Pt initially subplanted, the initial current was the smallest of all the electrodes. The current remained low during 20 additional narrow range CVs, but when the sample was scanned to oxidizing potentials, the HER activity increased dramatically, as shown by Figure 8B, which shows some of the CVs and the change in the HER current vs. CV cycle. Notably, The factor of ~30 increase in HER activity was largely irreversible in this case, i.e., the activity remained high in repeated narrow range CVs. The Pt₄/HOPG electrode deposited at 13 eV/atom (Figure S14) also showed a significant, irreversible increase in activity when cycled to oxidizing potentials.

Irreversible increases in HER activity occurred only for electrodes prepared at high deposition energies, for which the initial activity was low, presumably due to subplantation. The irreversible increase in HER current during cycling to oxidizing potentials is, therefore, attributed to emergence of subplanted Pt into electrolyte-accessible surface sites. It is conceivable that emergence of subplanted Pt into surface sites was simply due to enhanced diffusion under higher applied potentials, but we note that the potentials required to “activate” these electrode were sufficient to drive water oxidation of carbon to CO or CO₂, which is thermodynamically possible above ~0.6 V vs. RHE. Indeed, we previously showed that small Pt_n soft landed on glassy carbon electrodes were efficient catalysts for carbon oxidation by water.³⁰ As shown in the SI, small

oxidation features, possibly due to carbon oxidation were observed in the CVs to oxidizing potentials.

Mass activities and comparison to other Pt catalysts

Electrocatalysts are commonly compared in terms of either mass activities, i.e., currents normalized to the Pt mass present, or current densities, i.e., currents normalized to the electrochemically active surface area (ECSA). We report mass activities because we know that precisely 1.46 ng of Pt impacted on each electrode during deposition, providing an upper limit on the electrolyte-exposed Pt mass. ECSA is typically estimated by integrating the current associated with some reaction that is limited by the number of electrolyte-accessible Pt atoms, such as hydrogen underpotential deposition (H_{UPD}) or CO stripping. For example, it has been established that for polycrystalline Pt (Pt_{poly}), the integrated H_{UPD} current is equivalent to adsorption of ~ 1 H atom *per* exposed Pt atom,⁷ allowing ECSAs to be determined *assuming that the Pt surface has bulk-like H adsorption properties*.

That is a reasonable assumption for nanoparticles large enough to have surface coordination close to the bulk value, but not for sub-nano Pt_n clusters. For example, H_{UPD} measurements for soft-landed Pt_n/ITO ⁴ and Pt_n/FTO ⁵ found strongly cluster-size-dependent H/Pt ratios ranging up to >2 H/Pt. DFT showed that the H adsorption properties were affected by both the undercoordination and fluxionality of small clusters, and such effects are also expected for $Pt_n/HOPG$. Furthermore, DFT predicts that H can adsorb at both Pt and carbon defect sites on $Pt_n/HOPG$ (Figure 7). Similar considerations would apply to other surface adsorbates, i.e., surface-reaction-based approaches to ECSA determination are simply not reasonable for electrodes containing small clusters.

Figure 9 compares the mass activities at three different overpotentials (η) relative to the thermodynamic HER onset. In Figure 9A, background-subtracted HER currents were simply normalized to the 1.46 ng mass of Pt_n that impacted on each electrode, i.e., the activities are not corrected for either sticking probabilities or subplantation. Bars labeled with the just the Pt_n size and deposition energy designate activities for $Pt_n/HOPG$ prepared by deposition at those energies on SPI-1 grade HOPG. Mass activities are also shown for Pt_1 deposited at 50-60 eV and Pt_4 deposited at 13 eV/atom (52 eV total energy) on SPI-2 grade HOPG, showing values for both the as-deposited electrodes and after “activation” by cycling to oxidizing potentials (Figure 8). SPI-1

(magenta bars) is reported to have lower density of steps and other defects, compared to SPI-2 grade HOPG (orange bars).

For comparison, mass activities are also shown for samples prepared by soft landing 0.1 ML of Pt₄ and Pt₇ on FTO in UHV, and for Pt₇ soft landed on Ar⁺ sputter-damaged HOPG. To provide a familiar and easily replicated comparison system, we also show values for “Pt_{poly}”, i.e., HER currents for polycrystalline Pt normalized to the mass of the *electrolyte-exposed surface monolayer*. The surface monolayer mass was estimated from the integrated H_{UPD} current assuming adsorption of 1 H atom/exposed Pt atom.⁷ Note that the Pt_{poly} values would be upper limits on the mass activities for bulk-like Pt particles, because only a fraction of the Pt in such particles is in the surface layer.

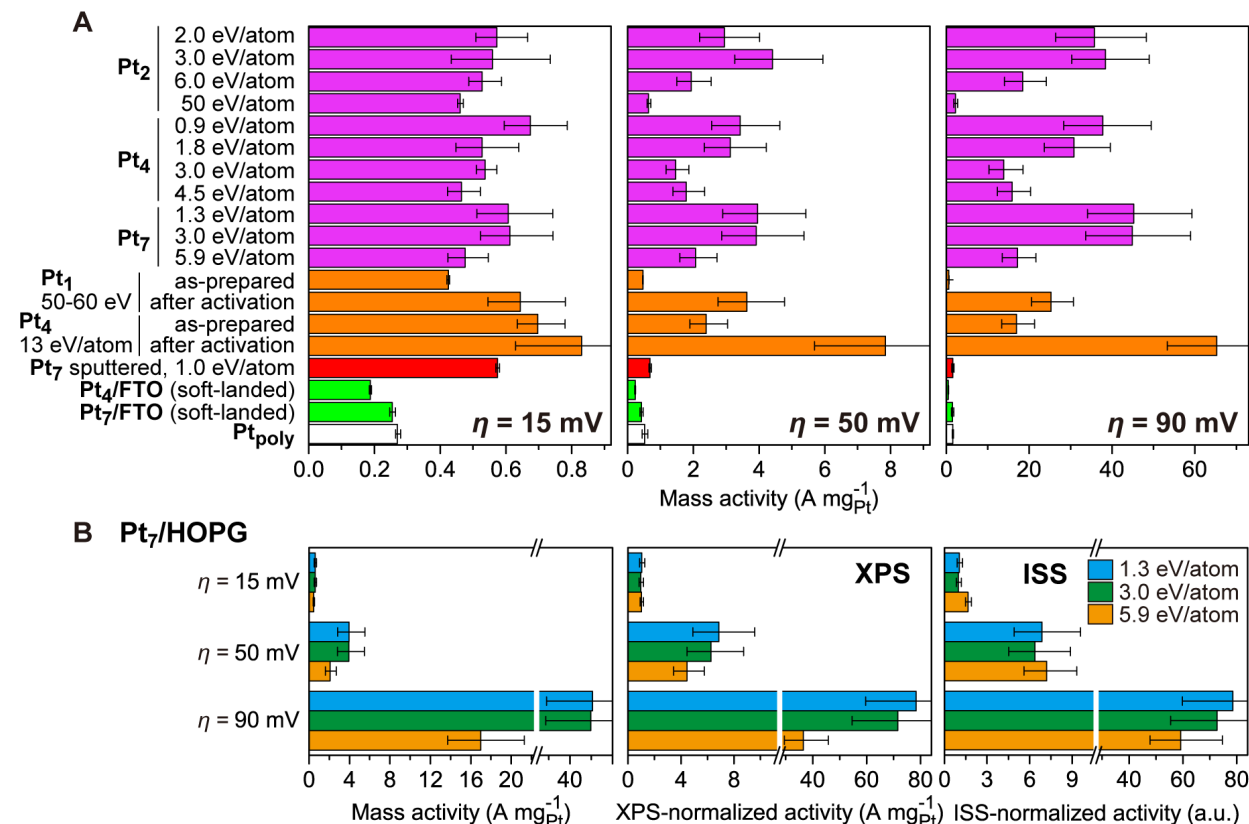


Figure 9. A). HER mass activities at 15, 50, and 90 mV overpotential (η), using the 1.46 ng mass of Pt impacting the HOPG, i.e., not correcting for sticking or subplantation. Also shown are values for Pt₄ and Pt₇ soft-landed on FTO, Pt₇ soft-landed on Ar⁺ sputtered HOPG, and the surface monolayer of polycrystalline Pt. B). Mass activities for Pt₇, comparing the activities based on the mass of Pt impacting the HOPG (left), the mass of Pt that stuck on the HOPG as probed by XPS (middle), and the mass of Pt on the surface, as probed by ISS (right).

At the two higher overpotentials, the mass activities depend strongly on deposition energy, with hard landed electrodes showing lower activities than soft-landed electrodes, especially for Pt₁ deposited at 50-60 eV and Pt₂ at 50 eV/atom. Indeed, the (uncorrected) mass activities for the soft-landed Pt_n/HOPG electrodes are an order of magnitude or more higher than those for Pt_n/FTO or the Pt_{poly} surface layer. Strong dependence on deposition energy is expected because we know that both sticking probability and subplantation are energy dependent. The lowest mass activities are associated with ~50 eV/atom impact energies, which the trajectories show to result in efficient sticking and subplantation, leaving little Pt on the surface. The fact that the mass activities for hard-landed electrodes increased after cycling to oxidizing potentials is attributed to initially subplanted Pt emerging into electrolyte-accessible sites, probably due to oxidation of overlying carbon. The mass activities for electrodes deposited at intermediate energies reflect both decreased sticking probability and the beginning of subplantation.

The use of XPS and ISS to approximately correct the mass activities for the effects of sticking and subplantation is shown in Fig. 9B for Pt₇/HOPG. The left frame simply replots the uncorrected data from Figure 9A, i.e., the mass activities are calculated based on the 1.46 ng mass of Pt that *impacted on the HOPG* during deposition. In the middle frame the currents are normalized to the mass of Pt *present in each sample*, i.e., to 1.46 ng • S, where S is the sticking probability estimated from XPS (Figure 1C). On that basis the deposition energy dependence is weaker, however, lower mass activity is still seen for the highest deposition energy. In the right frame, the currents are normalized to the mass of Pt *present in the surface layer*, estimated as 1.46 ng • S • Pt surface fraction (from Figure 1G), assuming that the Pt surface fraction is 1.0 at low deposition energies, where subplantation is energetically impossible. When only surface layer Pt is included, the activities at the higher overpotentials longer depend significantly on deposition energy.

At $\eta = 15$ mV, however, the situation is quite different. As shown by Figure 9A, the dependence of the (uncorrected) mass activities on deposition energy becomes quite weak at $\eta = 15$ mV, and very different from the dependence at higher η . In fact, because we know that electrodes prepared at the highest deposition energies would have had substantially less surface layer Pt present than the soft-landed electrodes, we can say that the low overpotential activity for the *surface layer* atoms in the hard-landed electrodes must have been substantially higher than the activity for soft-landed Pt_n/HOPG. The inherently high activity of hard-landed Pt_n at low

overpotential is shown in Fig. 9B, where at $\eta=15$ mV, the 5.9 eV/atom sample had significantly higher surface Pt mass activity than the softer-landed electrodes.

The obvious question is why the surface atoms in hard-landed Pt_n are more active than the surface atoms in soft-landed Pt_n . Pt_n soft landing would have deposited the cluster onto a mostly undamaged HOPG surface, resulting in weak cluster-surface binding. Imaging experiments done for clusters soft-landed on HOPG have shown extensive cluster diffusion leading to aggregation.^{12, 13, 14, 15} In contrast, our trajectories showed that under hard-landing conditions, Pt_n would have penetrated the surface (consistent with ISS experiments), leading to carbon defect creation, cluster fragmentation, and strong binding of small Pt species at carbon defects on or beneath the surface layer, stabilized against diffusion in either case.

Thus, the finding is that at low overpotential, the surface atoms in small defect-bound Pt species present in hard-landed Pt_n /HOPG are substantially more active than the atoms in the aggregated Pt_n structures formed by soft landing. High activity for small defect-pinned Pt species is consistent with the low DFT free energy barriers shown in Figure 7A. The implication is that the activity for Pt atoms in larger aggregated Pt structures is significantly lower, although still twice the activity of the surface layer atoms in Pt_{poly} .

There is an interesting relationship between the overpotential-dependent Pt_n /HOPG mass activities, and the numbers of electrolyte-accessible H adsorption sites, as determined from the integrated H_{UPD} currents, shown in Figure S15. The cluster size and deposition energy dependences of the H_{UPD} signal and the uncorrected mass activities at $\eta = 15$ mV (Figure 9A) are nearly identical, suggesting a correlation between HER activity and the availability of H atom adsorption sites. That correlation is no surprise, however, it is surprising that even the hardest-landed Pt_n /HOPG, with little surface-layer Pt, should have similar H adsorption properties to soft-landed electrodes where all the Pt is in the surface layer. The DFT results suggest a solution. Figure 7 shows that H atoms can adsorb and contribute to HER both at exposed Pt sites and at carbon defect sites created by Pt_n hard landing. Thus, the weak dependence of the H_{UPD} signal on deposition energy is tentatively attributed to H adsorption at carbon defects, the coverage of which should tend to increase with deposition energy, offsetting the decrease in surface Pt sites caused by subplantation. The similar deposition energy dependence of the $\eta = 15$ mV mass activities suggests that these C defect-adsorbed H atoms must also contribute significantly to the HER mass activities at low overpotentials, where the HER kinetics are slow even on Pt. The appearance of

strong deposition energy dependence at higher overpotentials suggests that as the HER kinetics at Pt sites becomes faster, the kinetics at C-defect sites must increase more slowly, such that HER at defect sites no longer contributes substantially.

One obvious question is how soft-landed Pt_n/HOPG electrodes can have mass activities significantly greater than that of the surface atoms in Pt_{poly} , given that the clusters in these samples almost certainly would have aggregated. We tentatively attribute the high activity to the nature of the aggregation process for clusters of refractory materials (like Pt) on weakly binding surfaces like HOPG. Aggregation in such systems tends to occur by Smoluchowski ripening, i.e., by diffusion and aggregation of intact clusters, forming elongated structures at steps and branched aggregates on terraces.^{14, 15, 31} Such aggregates preserve the low Pt-Pt coordination of the original small clusters to a much greater extent than would be the case for compact 3D nanoparticles. Thus, these aggregated cluster structures have HER activities more similar to that of small Pt_n species, rather than large 3D particles.

Another question is the extent to which isolated carbon defects, i.e., those with no Pt bonded to the defective carbon atoms, contribute to the HER activity. As noted above, DFT activation barriers were calculated for reaction of H atoms bound at carbon defects without attached Pt atoms and were found to be roughly double the barriers for H on Pt or on C atoms bound to Pt, suggesting that isolated defects, by themselves, do not contribute to the HER signals. To test the effects of isolated carbon defects experimentally, HER was also studied for an electrode prepared by first bombarding HOPG for 1 minute with 1 keV Ar^+ , sputtering carbon and creating defects, then soft landing Pt_7 at ~ 2 eV/atom energy. If carbon defects were highly active, either by themselves or with soft-landed Pt clusters binding on them, then this sample should have shown mass activity comparable to the activities for Pt_n hard landed on HOPG. Instead, as shown by the raw data in Figure S16 and the “Pt sputtered” value in Figure 9, the activity, except at the lowest overpotential, was lower than that for Pt_7 hard-landed on HOPG, and comparable to those for Pt_7 soft-landed on FTO or for the Pt_{poly} surface layer.

The activities for Pt_n/HOPG are substantially higher than those for Pt_n/FTO , and we propose that one contributing factor is transport. As shown in Figure S17 the clusters present in and on HOPG after energetic impacts are polarized. Pt atoms directly bound to C atoms for which the C-C bonding has been disrupted are oxidized (have positive Bader charge), whereas the Pt atoms exposed to electrolyte and not bound to C feature a partial negative charge. This charge

distribution suggests that the transport of protons from solution to the catalyst is electrostatically facilitated. Such polarization is not characteristic of Pt_n/FTO or Pt_{poly}.

Conclusions

We explored the deposition and subplantation dynamics for Pt_n impacting HOPG at variable energies, using a combination of size- and energy-selected cluster deposition experiments and DFT-based trajectory simulations. The sticking probability is significantly below 1.0 at low deposition energies, and the DFT simulations show that those clusters that do stick adsorb weakly on the intact HOPG surface. These presumably aggregate upon deposition, but aggregation is not feasible for trajectory analysis, nor were we successful in imaging the clusters due to a combination of electron beam effects and contaminated TEM grids. At high deposition energies, the simulations show efficient sticking but with substantial cluster fragmentation, subplantation, scission of both Pt-Pt and C-C bonds. Covalent bonds formed between the Pt species and carbon defects, which should tend to pin the clusters at the deposition site. The simulation results are consistent with the experiments, where XPS showed sub-unit sticking probabilities at low deposition energies, and efficient sticking at high energies, but with ISS implying substantial Pt subplantation, which also is correlated with low HER activity.

The HER mass activities for Pt_n/HOPG electrodes prepared by energetic cluster deposition were quite high compared both to Pt_n soft-landed on FTO, Pt_n soft-landed on sputter-damaged HOPG, and the surface atoms in Pt_{poly}. The exceptions were Pt_n/HOPG samples prepared at the highest energies, which had low initial HER activity attributed to subplantation of most of the Pt into sites inaccessible to electrolyte. If only the surface-accessible Pt atoms in the hard-landed samples are included in the calculation, their mass activities are also high, particularly at low overpotentials. Hard-landed electrodes with substantial subplanted Pt became considerably more active after a brief period of cycling to high potentials. The appearance of weak, broad oxidation features at high potentials for such samples suggests that this “activation” process may involve oxidative removal of carbon, exposing initially subplanted Pt.

The cluster size effects in this system are relatively weak. This partly reflects facile aggregation of the weakly-adsorbed clusters prepared by cluster soft landing, as has been observed previously.^{12, 13, 14} For the smaller, defect-bound Pt species prepared by hard landing, the lack of size effects is consistent with the DFT finding that the rate-limiting activation free energies are only weakly dependent on the Pt_n size and structure.

ASSOCIATED CONTENT

Supporting Information. Details of the experimental and computational methods, supporting data, explanations of analysis approaches, additional examples. (HER-PtnHOPG_SI.pdf). Python script for DFT structure generation (Str_Generation.zip) Geometric data for DFT structures in Figures 6 and 7 (Used_structures.zip). Numerical data underlying experimental figures (ExptDataTables.xlsx)

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