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Electrochemical Degradation of Pt₃Co Nanoparticles Investigated by Off-Lattice Kinetic Monte Carlo Simulations with Machine-Learned **Potentials**

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validate the wide applicability of our method by successfully applying it to Pt_3Ni and $Pt_3Co_{0.5}Ni_{0.5}$ nanoparticles. Our research serves as a guideline for developing MLPs for alloy electrochemical catalysts and lays the foundation for designing more durable and active fuel-cell catalysts.

KEYWORDS: off-lattice kinetic Monte Carlo simulation, machine-learned potential, fuel cell, Pt alloy nanoparticle, durability

INTRODUCTION

One of the main challenges in the wide implementation of fuel cells is the high activation barrier required for the oxygen reduction reaction (ORR) at the cathode, resulting from the strong double bonds in oxygen molecules.¹ To address this issue, considerable efforts are currently underway to discover an efficient catalyst capable of lowering the barrier.² Pt stands out as the most recognized catalyst due to its exceptional performance.³ However, its high cost impedes a wide implementation.⁴ As such, the focus in the practical use of the fuel cell is primarily on reducing Pt amounts in catalyst materials.

A promising strategy to reduce the Pt loading involves alloying Pt nanoparticles with 3d transition metals such as Co, Ni, and Fe,⁵ which also amplifies the catalytic activities, thereby fulfilling the standards established by the U.S. Department of Energy.⁶ On the other hand, the inclusion of 3d transition metals often compromises durability. Vumerous studies have been conducted to identify the major factors affecting durability, focusing on the influence of microstructures such as size,⁸ shape,^{9,10} and atomic ordering.¹¹⁻¹³ However, it is challenging to establish a detailed atomistic understanding of the degradation mechanism solely through

experiments due to the limitations in synthesis controllability and resolution of analytic tools.¹⁴ For instance, the relative stability between ordered and disordered phases of Pt-based alloy nanoparticles is still under debate: ref 15 reports that disordered Pt-Co nanoparticles exhibit higher durability than the ordered ones, while contradictory findings are presented in ref 16. This contradiction may originate from the fact that the control of atomic ordering often accompanies the change of particle size,¹⁷ which complicates the task of quantifying the individual contribution of each factor.

Theoretical methods have provided atomistic insights into the degradation of the ORR catalysts. In particular, density functional theory (DFT) calculations have been used to explore the dissolution potential of nanoparticles across diverse structures.¹⁸⁻²¹ However, due to their large computational cost, these studies employed rather simplified nanoparticle

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models: using small nanoparticle sizes,¹⁸ symmetrizing nanoparticle shapes,²¹ or assuming layer-by-layer dissolution.^{19,20} To overcome this limitation, kinetic Monte Carlo (kMC) simulations have been coupled with efficient energy calculators such as simple parameterized models,²² empirical force fields,²³ or cluster expansion method.^{24–26} These studies, however, restricted atomic positions to fixed lattice sites (known as onlattice models) during kMC simulations owing to the limited adaptability of empirical models in describing diverse atomic structures. Consequently, the derived structures displayed jagged rather than smooth shapes typically observed experimentally.^{27,28} To enable simulations beyond an onlattice model, an interatomic potential is required to be capable of accurately evaluating the potential energy surface for complex geometries that emerge during off-lattice simulations.

Machine-learned potentials (MLPs) have recently gained attention due to their low computational cost, flexible applicability over diverse structures, and accuracy comparable to DFT calculations,²⁹ which find immediate applications in various domains like crystal structure prediction,^{30,31} phase change materials,³² nanocrystals,³³ and catalysts.^{34,35} MLPs have also been utilized to examine the stability of Pt-alloy nanoparticle catalysts: in ref 36, an MLP was used to identify the optimal atomic distribution of Pt–Cu–Ni alloy nanoparticles using Monte Carlo (MC) and molecular dynamics (MD) simulations. However, the stability of nanoparticles was assessed only on defect-free models without considering the defective and distorted surfaces of realistic nanoparticles.

In this study, we develop an MLP to simulate the degradation process, encompassing dissolution and vacancy migration, in Pt_3Co nanoparticles known for their high stability and activity.³⁷ The developed MLP is validated to accurately emulate the energetics associated with vacancy formation and migration across various compositions and shapes of nanoparticles. Dissolution trends of realistic-size nanoparticles (up to 4 nm) are analyzed through off-lattice kMC simulations, with the MLP evaluating the energies and activation barriers of intermediate structures. We investigate the effects of size, shape, and atomic ordering on durability and provide design principles for achieving both high durability and activity. Finally, we demonstrate that the developed method can be successfully applied to other alloy systems, such as Pt_3Ni and $Pt_3Co_{0.5}Ni_{0.5}$.

COMPUTATIONAL DETAILS

Machine-Learned Potential. We adopt Behler–Parrinello-type neural network potential (NNP)³⁸ with input features encoded by an atom-centered symmetry function.³⁹ The feature generation and training of the NNP are conducted using the SIMPLE-NN package.⁴⁰ To achieve the balance between computational cost and accuracy, the parameters of symmetry function vectors are chosen by CUR decomposition.⁴¹ This method finds low-rank approximation ($\tilde{\mathbf{A}}$) of the original feature matrix (\mathbf{A}) as follows

$$\mathbf{A} \approx \tilde{\mathbf{A}} = \mathrm{CUR} \tag{1}$$

where U denotes the mixing matrix, and C and R are rows and columns of the original feature matrix, respectively. The component numbers of the symmetry function vectors for both Pt and Co are 32. The cutoff radius for calculating the symmetry function is set to 6 Å. The reference data is split into training and validation data sets with a ratio of 9:1. The energies, forces, and stresses of reference structures are computed through DFT calculations employing the VASP code,⁴² with PBE exchange–correlation functional.⁴³ A cutoff energy of 300 eV is chosen for the plane-wave basis set, and a k-point spacing of 0.4 Å⁻¹ is chosen. These settings ensure convergence criteria of 10 meV/atom and 0.1 eV/Å for energy and force, respectively. For structures involving Co atoms, spin-polarized calculations are performed by assuming ferromagnetic spin configurations. We exclude the solvation effect after confirming its negligible impact on the surface energy and the vacancy formation energy (see Table S1 and Figure S1). For slab and cluster configurations, a vacuum layer of at least 8 Å is added. NVT MD simulations are conducted for 3 ps at 600 K by DFT calculations, with a time step of 2 fs.

Off-Lattice Kinetic Monte Carlo Simulation. We employ off-lattice kMC methods to simulate the realistic degradation process of nanoparticles. In the kMC simulation, a system evolves to the next local minima by selecting an event based on the probability proportional to the reaction rate (k_i) , which is given by

$$k_i = \nu_i \exp\left(-\frac{E_{a,i}}{k_{\rm B}T}\right) \tag{2}$$

where ν_i and $E_{a,i}$ indicate the attempt frequency and activation energy of the *I*-th event, respectively, and k_B and *T* are the Boltzmann constant and temperature, respectively. The event table consists of (1) surface vacancy formation and (2) vacancy migration for the emulation of the atomic dissolution and rearrangement, respectively. We neglect the redeposition of dissolved atoms, as its reaction rate is considerably lower compared to these reactions.²⁸

For modeling dissolution processes, we obtain the activation barrier from Brönsted–Evans–Polanyi (BEP) relation⁴⁴ using surface vacancy formation energy, instead of directly calculating the activation energy of the dissolution trajectory. Note that explicit dissolution simulations are challenging due to the large degree of freedom and the alteration in work function during the electrochemical process,⁴⁵ while there are ongoing developments in this field.^{46–49} The parameters for the BEP relation are extracted from literature, where they were determined through fitting to replicate the experimental results^{50–52} (see Figure S2 for sensitivity test). Note that realistic factors such as the electrolyte effect and the influences from the oxygenated species are not considered in this work. Even so, the fitting process of the BEP parameters would implicitly reflect such factors.

For diffusion events, an initial state and a final state are defined by employing a simple grid-based search with singleatom hopping rather than exhaustive approaches such as the dimer method⁵³ or the kinetic activation-relaxation technique.⁵⁴ The activation energies for diffusion reactions are calculated on the fly by the nudged elastic band (NEB) method.⁵⁵ The search methods are described as follows (see Figure 1a): first, we generate a spherical surface grid using a Fibonacci lattice⁵⁶ (refer to Figure S3) with a point density of 3.65 $Å^{-2}$, centered around the target atom. The radius of the grid is set at 2.8 Å, which is approximately equal to the average bond length. Next, the grid points that are too close to neighboring atoms (<2.2 Å) or have a low coordination number (≤ 4) are filtered out from the candidates. Note that the threshold of 2.2 Å is determined by the radial distribution function of disordered Pt-Co alloy (see Figure S4) and the threshold for coordination number, set at 4, is selected after



Figure 1. Diffusion process for kMC simulations. (a) Schematic representation of the path-searching algorithm. The red atoms stand for the target atom, and the black dots represent the spherical grid points for trial hopping. The yellow spheres represent the candidates for hopping sites. Then, structural relaxation is done to obtain the final structures. (b) Example of initial, activation, and final states for the diffusion process.

the structural relaxation test (see Figure S5). The remaining grid points within the same local basin are merged into one activation site. Two grid points are considered to be in the same local basin if the angle between their vectors, extending from the origin to each grid point, is less than 30° . The choice of 30° angle threshold is inspired by ref 57 which suggested the angle threshold as half of the minimum angle between the configuration vectors of unique transition states. Similarly, we take half of the smallest angle between the two nearest neighbors in an FCC lattice, which is 60°. Lastly, structural optimization is performed for each candidate configuration to check whether the target atom returns to the initial state. Figure 1b shows an example of diffusion events: it is shown that the search algorithm successfully finds the local basin, even in the case in which it deviates from a simple on-lattice site. The calculation results are accumulated in the database and reused when the same event occurs. Note that two events are defined as identical if the sets of the coordinates of neighboring atoms (within 6 Å) around the target atoms are identical (within tolerance criteria of 1 Å). Although distinguishing between two events using this definition is permutationally and rotationally variant, it remains effective as identical events predominantly occur in sequential simulation steps. In order to prevent the system from being trapped within a superbasin with minimal time evolution, the rate of a specific event is reduced by a factor of 2 every time it is consecutively sampled nine times, which ensures the escape probability from a superbasin remains within a 20% error margin.58

The values and calculation methods for the attempt frequency and barrier energy are summarized in Table 1. While attempt frequency for dissolution events is taken from ref 59 as 10^4 Hz, one for diffusion events is chosen to be 10^6 Hz in this study. The attempt frequency for diffusion events is far smaller than the Debye frequency of 1×10^{13} Hz, which is widely used in a solid system. However, with such high frequency, the kMC simulation would spend most of the time

Table 1. Attempt Frequency Values and Methods for Calculating the Barrier Energy for Each ${\rm Event}^b$

event	attempt frequency (constant)	barrier energy (on the fly)
dissolution	10^4 Hz^a	BEP relation
diffusion	10 ⁶ Hz	NEB method

^{*a*}From ref 59. ^{*b*}Whether the values are constant or calculated on the fly is written in parentheses.

on the vacancy hopping near the equilibrium state with little time evolution. To reduce the attempt frequency, we conduct a convergence test as shown in Figure S6 and find that the temporal behavior of dissolution rates becomes similar when the attempt frequency is above 10^6 Hz. Thus, we choose this value as the attempt frequency for vacancy migration.

The initial structures of the kMC simulations are constructed through atom-swapping Monte Carlo (MC) simulations to build thermodynamically plausible structures. The MC simulation begins with Pt_3Co random configurations, exchanging atomic positions with their first nearest neighbors based on the Metropolis criterion.⁶⁰ The MC simulations are terminated when the surface Pt ratio becomes about 90% following the experimental measurements (typically, 85–100%).^{61–64} We find that the surface Pt ratio of the initial structures has a considerable impact on the dissolution rate of nanoparticles. Even so, we check that the change in the surface Pt ratio does not alter the overall trends regarding the relative stability among various nanoparticles and thus does not affect the main conclusions of this study.

All the above procedures, including MC and kMC, are conducted by in-house code, MINK (Machine learning INteratomic potential with Kinetic Monte Carlo) coupled with the LAMMPS package.⁶⁵ All kMC simulations are repeated 5 times to analyze the statistical variance. Further details of the kMC simulations are described in the Supporting Information.

RESULTS AND DISCUSSION

Training and Validation of Machine-Learned Potential. We develop a Behler-Parrinello-type NNP for Pt-Co alloy nanoparticles trained on the reference structures obtained from DFT calculations. Figure 2 illustrates the simulation model for Pt₃Co alloy nanoparticles, along with the structures included in the training set used for constructing the NNP. The Pt₃Co nanoparticle structure consists of four distinct parts: bulk, surface, edge, and corner. During degradation processes, these structures undergo applied strain and the formation of various vacancy configurations. To account for these variations, the training set encompasses (1) strained bulk crystals, (2) MD trajectories at 600 K, (3) NEB trajectories for vacancy migrations, and (4) the relaxation trajectories of multivacancies in bulk, slab, and cluster structures across the compositions of $Pt_{1-x}Co_x$ (x = 0, 0.1, 0.2, 0.3, 0.4). The clusters are created from cutting nanoparticles (truncated octahedrons, icosahedrons, cuboctahedrons, and octahedrons) with a cutoff radius of 12 Å centered around the selected vertex atoms.⁶⁶ To enhance the electronic convergence of DFT calculations, atoms with coordination numbers of less than six are removed. In order to efficiently sample diverse defect configurations, we ensure that the training structures in the same category (see Table S2) do not contain the same local environments of vacancies, which are defined by the composition of the nearest-neighbor atoms. (We confirm



Figure 2. Schematic description of the simulation model and training configurations for the Pt_3Co nanoparticles. The gray, blue, and orange atoms stand for Pt, Co, and vacant sites, respectively.

that when the nearest-neighbor configurations are fixed, there is only about a 0.1 eV variation in the vacancy formation energies; see Figure S7.). To check whether this approach rather results in under-sampling configurations that frequently emerge, we examine the uncertainty values⁶⁷ for the structures that emerge during the kMC simulation (see Figure S8) and confirm that the uncertainty values remain relatively low across all energy ranges. In total, we sampled 4576 configurations comprising 514,449 local atomic environments (see Table S3).

The trained NNP exhibits root-mean-square errors (RMSEs) of 4.46 meV/atom, 0.13 eV/Å, and 6.72 kbar for energy, force, and stress, respectively, for the validation set (Figure S9). The RMSE values for the training set fall within a similar range, indicating the absence of overfitting. To assess the coverage of NNP over the compositions of $Pt_{1-x}Co_x$ ($0 \le x$)

 \leq 0.5), we evaluate its accuracy for random bulk configurations and intermetallic compounds (PtCo, Pt₃Co, and Pt), as shown in Figure 3a. The results demonstrate that the NNP accurately predicts energy values in reasonable agreement with the DFT across the relevant compositions. Furthermore, we test the accuracy of the NNP in predicting surface vacancy formation energies (Figure 3b) and migration barriers (Figure 3c) for the atoms in the surface or subsurface on randomly generated slab structures for (100) and (111) planes at a Pt₃Co composition. The NNP shows good accuracy for both vacancy formation energies (R^2 of 0.938 and RMSE of 0.136 eV) and migration barriers (R^2 of 0.847 and RMSE of 0.227 eV) compared to DFT references. Note that the modified embedded atom method (MEAM) potential⁶⁸ exhibits significantly larger errors (0.381 and 0.835 eV for vacancy formation and migration barriers, respectively, as shown in Figure S10).

Figure 3d displays the test results for the accuracy of the NNP compared to DFT on nanoparticles of different sizes and shapes. It can be seen that the error diminishes with an increasing radius. Specifically, nanoparticles with a diameter less than 0.9 nm exhibit a relatively large error, exceeding 0.25 eV/atom. To check if this trend stems from significant errors in undercoordinated atoms (e.g., edges and vertices) due to insufficient sampling, we estimate the uncertainties using a neural network ensemble (see Figure S11).⁶⁷ Except for the nanoparticles smaller than 0.9 nm, the uncertainties of both under-coordinated and bulk atoms remain within the threshold range established by the training set. This suggests that the errors are not centered on undercoordinated atoms. The large errors in small nanoparticles might be attributed to the presence of highly strained atoms, which are not explicitly included in the training set. In fact, as shown in Figure S12, we observe that a large portion of small nanoparticles have high uncertainty values. However, this error diminishes significantly when the diameter exceeds 1 nm, the size of interest in this study.



Figure 3. Performance test to evaluate the accuracy of NNP. (a) Energy comparison between NNP and DFT for random $Pt_{1-x}Co_x$ ($0 \le x \le 0.5$) bulk configurations and intermetallic compounds. Correlation between DFT and NNP energies for (b) vacancy formation and (c) vacancy migration barrier on (100) and (111) surfaces. (d) NNP errors depending on the size of the nanoparticle. (e) Time evolution of NNP and DFT energies for the configurations obtained from kMC simulation with NNP for truncated octahedron Pt_3Co nanoparticle with an applied voltage of 0.8 V_{SHE} at 350 K. The simulation is performed for 588 steps (10% loss of total atom), and then DFT energies are evaluated on the snapshots selected every 10 steps after the structure optimization.



Figure 4. Impacts of microstructures on the degradation ratio of Pt_3Co nanoparticles. (a) Time evolution of dissolution ratio of various sizes of truncated octahedron Pt_3Co nanoparticles. The dissolution ratio is defined as a ratio of the number of dissolved atoms to that of the initial total atoms. (b) Dissolution ratio after 24 h as a function of diameter. (c) Time evolution of dissolution ratio of various shapes of Pt_3Co nanoparticles. (d) Time evolution of dissolution ratio of ordered, disordered, and core/shell Pt_3Co nanoparticles. In (a,c,d), the shaded area in the plot represents the standard deviation, and the initial and final atomic structures are displayed on the right sides of the plot, respectively. All initial and final structures are cut by a quarter to display their internal atomic arrangements. In all simulations, the applied voltage and temperature are set to 0.8 V_{SHE} and 350 K, respectively.

As a final test, we ran the kMC simulations with NNP on a truncated octahedron Pt_3Co nanoparticle, followed by DFT calculations after structure optimization (Figure 3e). The energies obtained from NNP and DFT calculations are referenced to the energy of the first snapshot of the kMC simulation. The NNP and DFT energies are in reasonable agreement for all trajectories. We also confirmed the accuracy of the NNP in kMC simulations using other nanoparticle shapes with single-point DFT calculations (Figure S13).

Design Principles for Pt₃Co Nanoparticles. To identify design principles for Pt₃Co nanoparticles, we analyze the influence of size, shape, and atomic ordering on degradation performance using off-lattice kMC simulations with the NNP. First, we examine the impact of size on the degradation behavior of Pt₃Co nanoparticles. While it is well-known that larger nanoparticles exhibit increased stability,⁶⁹ the exact quantity of the contribution from size remains unclear because the control of size often accompanies the change in other factors such as composition.⁷⁰ Therefore, we study the effect of size independently using kMC simulations with Pt₃Co truncated octahedron nanoparticles. Figure 4a depicts the time evolution of the dissolution ratio under fuel cell operating conditions (voltage = $0.8 V_{SHE}$ and temperature = 350 K) for nanoparticles of varying sizes along with the corresponding initial and final structures on the right side. As expected, the dissolution ratio decreases with increasing size; after 50 h of the reaction process, 2.52, 3.28, and 4.04 nm nanoparticles lose 40, 23, and 12% of their atoms, respectively. The dissolution ratio as a function of the nanoparticle size is plotted in Figure 4b. Notably, the dissolved amounts of Pt and Co across all sizes indicate that the dissolution ratio of Co is approximately

three times larger than that of Pt. For a quantitative analysis, we fit the total dissolution ratio to a form derived from the Gibbs–Thomson equation⁷¹ (see the Supporting Information for the derivation)

total loss (%) at 24 h=
$$\frac{15 \text{ nm}}{d} \exp \frac{4.21 \text{ nm}}{d}$$
 (3)

where d represents the diameter of the nanoparticle.

On the right side of Figure 4a, we observe that the final structures display distorted surface morphologies compared to the original angular shape, primarily due to the presence of surface defects, resulting in a more rounded shape. This surface rounding phenomenon observed after electrochemical activation agrees with the experimental observations made using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM).²⁸ To further clarify the geometry evolution of Pt₃Co nanoparticles, we calculate the angular distribution function (ADF) of the octahedral nanoparticle in Figure 5a. The ADF of the initially relaxed structure before kMC simulation (blue line), the final structure (orange line), and the ideal FCC octahedron are compared. We note an evident broadening of the peaks, even from the initial structure, due to the optimization. This broadening becomes more significant after a kMC simulation. In particular, the final kMC structure exhibits a markedly widened peak around 120° (red arrow), which is attributed to the 5-order ring formed due to the distortions near vacancies (see Figure 5b for atomic configurations). We also present the ADF values of surface atoms for the icosahedral nanoparticle in Figure 5c. We observe emergence of a broad peak at 90° (red arrow) from the final kMC structure, absent in the on-lattice structure



Figure 5. Angular characteristics of reduced octahedral Pt₃Co nanoparticle. (a) ADF of nanoparticles of the surface atoms of the octahedral nanoparticle. (b) Atomic structure associated with the broadened peak near 120° as indicated by the red arrow in (a). (c) ADF of nanoparticles of surface atoms of the icosahedral nanoparticle. (d) Atomic structure associated with the broadened peak near 90° as indicated by the red arrow in c. The red Pt atoms in b and d correspond to the configurations that result in the ADF values pointed by red arrows in a and c. The dashed lines in (a,c) stand for the angles found in the FCC octahedron and icosahedron, respectively.

and the initial kMC structure. The corresponding atomic structure is shown in Figure 5d. Note that these distorted structures cannot be captured from the existing on-lattice kMC approaches because they do not allow for optimization during the simulation. $^{22,24-26}$

We also examined the bond-length differences between the structures before and after kMC simulations. Figure 6a,b shows



Figure 6. Variation in the bond length and composition of Pt_3Co nanoparticles before and after kMC simulations. Bond length of surface and subsurface atoms (a) before and (b) after kMC simulations for varying sizes of octahedron nanoparticles. Content of Co atom as a function of distance from the surface (c) before and (d) after kMC simulations for 3.28 nm nanoparticles. The green (red) dashed line in (a,b) represents the Pt–Pt (Pt–Co) bond length in the Pt (Pt₃Co phases). In (c,d), the red dashed line indicates the Co composition in Pt₃Co (i.e., 0.25).

the Pt-Pt and Pt-Co bond lengths on the surface and subsurface before and after kMC simulation, respectively. In both structures, the Pt-Pt bond length on the surface (approximately 2.70 Å) is smaller than that of Pt crystal (2.80 Å) and Pt₃Co crystal (2.74 Å), which might be attributed to the influence from the high Co concentration of the subsurface (see Figure 6c,d). Interestingly, after kMC simulations, the nanoparticles exhibit a slight reduction in the Pt-Pt bond length at the surface. Concurrently, we observe an elongation in both the Pt-Co and Pt-Pt bond lengths in the subsurface layers. This trend is likely a consequence of the selective dissolution of Co atoms from surface sites. As Co atoms are depleted primarily from edge and vertex locations, the adjacent Pt atoms experience reduced coordination numbers, leading to a tighter Pt-Pt binding at the surface. In contrast, the increase in average surface bond lengths can be rationalized by disappearance of Pt-Co bonds shorter than Pt-Pt bonds.

To investigate the effects of nanoparticle shape on durability, we compare dissolution rates of truncated octahedron, icosahedron, cuboctahedron, and octahedron nanoparticles of similar sizes (approximately 3.3 nm), as shown in Figure 4c. The durability ranking is icosahedron > octahedron > truncated octahedron > cuboctahedron. This trend is consistent with the trend in (111) surface coverages, where the ratios of the (111) surface area in the total surface area are 1.0, 1.0, 0.76, and 0.37 for icosahedron, octahedron, truncated octahedron, and cuboctahedron, respectively. This is attributed to the higher vacancy formation energies on (111) surfaces compared to (100) surfaces (see Figure 3b), which aligns with the experimental observations obtained through inductively coupled plasma mass spectrometry (ICP-MS).⁷² The distinct durability between octahedrons and icosahedrons, despite having the same (111) surface coverage, stems from the varying number of neighboring atoms at the edge sites; octahedrons have 7 neighboring atoms at the edge sites, while icosahedrons have 8. As a result, icosahedrons exhibit lower vacancy formation energies on the edge sites compared with octahedrons (see Figure S14). It should be noted that the previous DFT study reported a stability trend of truncated octahedron > cuboctahedron > icosahedron,¹⁸ which differs from our findings. However, ref 18 solely assessed relative stability based on the dissolution potential of the vertex atoms, which is distinct from the edge and facet sites.²¹ The comparison between our study and ref 18 indicates that the contributions from facet and edge sites have a more significant impact on degradation than those from vertex sites.

To examine the influence of atomic orderings on durability, we compare the dissolution rates of nanoparticles with ordered, disordered, and core/shell ($Pt_{0.75}Co_{0.25}/1$ ML of Pt) structures, as shown in Figure 4d. Note that it is challenging to make a fair comparison by experiments because the control of atomic orderings by heat treatment usually accompanies the change in the nanoparticle size.¹⁷ Therefore, the relative durability between nanoparticles of ordered and disordered phases is still controversial.^{15,16} We observe that the distinction between ordered and disordered phases is not particularly significant, especially when compared with the distinction between these phases and the core/shell structure. This is because the surface of the ordered phase also becomes disordered after activation (see the final structure in Figure 4d) due to the surface rounding effect (see above).

To summarize, we have identified the impact of size, shape, and atomic ordering on the durability of Pt₃Co nanoparticles. Our findings reveal that increasing the nanoparticle size and (111) surface coverage enhances durability, while the atomic ordering of the core phase has a relatively minimal effect compared to other factors. Additionally, the (111) facet exhibits higher catalytic activity compared to different facets,⁷² making the icosahedron shape ideal in terms of both activity and durability. Enlarging the nanoparticle size enhances durability, but it also leads to a decrease in the surface-tovolume ratio by 1/d (d: diameter), resulting in a proportional reduction in catalytic activity. Conversely, reducing the nanoparticle size increases the surface-to-volume ratio, but it also increases the degradation rate and eventually reduces the surface area. The reduced surface area (SA) relative to the initial surface area due to the degradation can be derived from the total volume loss (eq 3) as follows

SA ratio =
$$\left(1 - \frac{0.15 \text{ nm}}{d} \exp \frac{4.21 \text{ nm}}{d}\right)^{2/3}$$
 (4)

We define the figure of merit (FOM) as a multiplication of these two factors

FOM =
$$\frac{1}{d} \times \left(1 - \frac{0.15 \text{ nm}}{d} \exp \frac{4.21 \text{ nm}}{d}\right)^{2/3}$$
 (5)

where this value is proportional to the surface-to-volume ratio after activation, and thus represents the effective catalytic activity. Figure 7 shows the FOM as a function of the nanoparticle size. The optimal catalytic performance is attained at a diameter of 2.5 nm.



Figure 7. Activity factor, durability factor, and overall FOM as a function of nanoparticle diameter. The activity factor is defined as 1/d, and the durability factor and FOM are defined as eqs 4 and 5, respectively.

Although not addressed above, the structural changes during dissolution, yet such changes, can influence catalytic performances. While it is possible to determine catalytic performances directly from atomic structures using additional machine-learned models, as indicated in,^{74,75} such studies would be beyond the scope of this work. Instead, for a simple assessment, we examine the Pt–Pt bond length on the surface due to its established correlation with the activation barrier of ORR.⁷⁶ As illustrated in Figure 6a,b, the Pt–Pt bond length at the surface is lower than that of Pt crystal, so the catalytic activity of Pt₃Co is expected to show higher activity than pure Pt nanoparticle. We also find that there is a minimal difference in this bond length after kMC simulations. However, atypical surface structures created during the dissolution, such as the 5-

order rings shown in Figure 5b, could significantly impact the catalytic performance. An in-depth study on the catalytic properties of such distorted structures will be conducted in future studies.

Extending the Elemental Systems. So far, we have studied the durability of the Pt₃Co alloy nanoparticles. The question remains whether the developed method is applicable to other Pt alloy systems with 3d metals, such as Ni, Cu, and Fe, including ternary compositions.⁷⁷ For the test, we train the NNPs for Pt₃Ni, and Pt₃Co_{0.5}Ni_{0.5} compositions and check the accuracy. To expedite the process, we change Co atoms in the original training set into Ni completely (partially) for the Pt₃Ni $(Pt_3Co_{0.5}Ni_{0.5})$ system to generate the training set. The NNPs of both systems are well-trained with low RMSEs (energy <10 meV/atom and force <0.3 eV/Å; see Table S4). The trends in durability in relation to the size, shape, and atomic ordering of Pt₃Ni nanoparticles are also similar to those of Pt₃Co nanoparticles (see Figure S15a-c). To note, we assume that the BEP parameters of Co and Ni are identical due to their similar electrochemical characteristics.⁷⁸ The durability of Pt₃Ni nanoparticles marginally surpasses that of Pt₃Co nanoparticles under the same condition, which is in good agreement with the experiments.⁷⁸ In addition, Pt₃Co_{0.5}Ni_{0.5} nanoparticles also demonstrate slightly enhanced durability compared to Pt₃Co (see Figure 8). The comprehensive investigation into the variance in composition extends beyond the scope of this study and will be the subject of future studies.



Figure 8. Time evolution of dissolution ratio of Pt–Co, Pt–Ni, and Pt–Co–Ni system. The shaded area in the plot represents the standard deviation, and the initial and final atomic structures are displayed on the right sides of the plot, respectively. All initial and final structures are cut by a quarter to display their internal atomic arrangements. In all simulations, the applied voltage and temperature are set to 0.8 $V_{\rm SHE}$ and 350 K, respectively.

Our method requires the BEP parameters obtained from the experiments. The ab initio computation of the activation barriers in electrochemical reactions is a formidable task due to the intricate nature of atomic environments and the hurdles faced when incorporating electrode potentials in the first-principles calculations (i.e., grand-canonical calculations). We note that considerable efforts are being made to tackle each of these challenges.^{46–49} Additionally, advancements are also being made in directly simulating solvent environments and electrochemical reactions using MLPs.^{79–84}

CONCLUSIONS

In summary, we have demonstrated that NNP combined with off-lattice kMC simulations can be an effective tool to

accurately describe the degradation process of real-scale nanoparticles. We systematically develop the NNP for Pt_3Co alloy nanoparticles based on the reference data obtained from DFT calculations, and the NNP yields reasonable accuracy. Through kMC simulations with the NNP, we investigate the influence of size, shape, and atomic ordering, leading to the derivation of design principles. Furthermore, we validate the applicability of our method to other elemental systems. We propose that the same approach employed in this study can be utilized to derive design principles for a wide range of nanoparticles. Thus, we postulate that this work contributes to the advancement of fuel cell technology and provides insights for the development of active and durable catalysts.

ASSOCIATED CONTENT

9 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c04964.

The effect of solvation on surface energy and vacancy formation energy, details of off-lattice kMC simulation, details of the training set of NNP, training quality of NNP, performance test of MEAM potential, uncertainty analysis of nanoparticles, single-point DFT calculations on the various shapes of nanoparticles, derivation of total loss ratio, edge vacancy formation energy profiles of icosahedrons and octahedrons, and kMC simulation results for Pt_3Ni (PDF)

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Notes

The authors declare no competing financial interest.

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