“Inverse Strain Effect in Atomic Scale”—Enhanced Hydrogen Evolution Activity and Durability in Cu-Substituted Palladseite

Saurav Ch. Sarma,^{†,‡} Vidyanshu Mishra,^{†,‡} K. A. Ann Mary,[†] Soumyabrata Roy,^{†,‡} and Sebastian C. Peter^{*,†,‡}

[†]New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India

[‡]School of Advanced Materials, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India

S Supporting Information

ABSTRACT: Since the preceding decade, strain engineering has been playing a vital role in modifying the activity of electrocatalysts. Incorporation of tensile strain into a Pd-based system usually requires substitution with larger atoms (usually a third row expensive transition metals). This work provides a unique strategy of introducing tensile strain by the substitution of small and low cost copper atoms (inverse strain effect) at the palladium sites of Pd₁₇Se₁₅. The Pd atom being in the +2 oxidation state adsorbs hydrogen very weakly, and Se, in its elemental state, binds weakly to H* adsorbate. However, the presence of Pd modulates the electronic structure of Se to have ΔG_{H^*} close to 0 and favors the progress of the reaction. Cu substitution further lowers ΔG_{H^*} , thus favoring the reaction. This unique synergistic effect between the two processes is accountable for better activity, high stability of 30 000 cycles and significantly high turnover frequency of 126.3 s⁻¹ for (CuPd)₁₇Se₁₅.

For several decades, a thrust exists within the scientific community to move toward the hydrogen economy. Hydrogen, being the environmentally cleaner source of energy, solves the pressing problem of carbonaceous emissions due to burning of conventional fossil fuels. The key to the success of the hydrogen economy lies in the cost-effective production of hydrogen, one of the best routes of which is through electrolysis of water. However, the state-of-the-art catalyst Pt/C hinders the long-term and extensive commercialization of water electrolyzers because of its low abundance and high cost. Thus, the demand for cheaper, efficient, and sustainable alternatives to Pt has ushered in a fast-evolving area of catalyst engineering where many innovative designs have already shown promising potential to compete with the state-of-the-art Pt catalyst toward electrochemical half-cell reactions. Activity and stability are the two important aspects of choosing an electrocatalyst.

It is well-known that the electrochemical activity of a catalyst can easily be altered by tuning the *d*-band center of the catalyst^{1–4} through several chemical and structural modifications such as by varying particle size, inducing strain through doping, substitution, intercalation, and creating overlayers and

interfaces.^{4–7} Of the several approaches used to tune the *d*-band center and consequently enhance the electrocatalytic performance of a catalyst, inducing strain has proven to play a significant role. Application of strain (tensile/compressive) shifts the *d*-band center toward or away from the Fermi level and thus strengthens or weakens the metal–adsorbate bond.⁴ The importance of the metal–adsorbate bond can directly be assessed from the Sabatier principle, which states that the bonding should be neither too strong nor too weak.⁸ Yan et al. directly demonstrated the effect of tensile and compressive strain on electrocatalytic activity of WC toward the hydrogen evolution reaction (HER).⁹ Similarly, Zhu et al. induced tensile surface strain in Co₉S₈/MoS₂ core/shell nanocrystals by changing the MoS₂ layer thickness from 5 to 1 L.¹⁰ Incorporating strain through substitution or doping is also prevalent in literature. For example, ultrathin Pt–M (M = Ni, Co, Fe),¹¹ RuP₂@NPC,¹² W(Se_xS_{1–x})₂,⁵ Zn-doped Co₃S₄,¹³ Co-doped MoS₂/F-ITO,¹⁴ MoS₂@Pt,⁶ Mo-doped W₁₈O₄₉,¹⁵

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and Co-doped NiSe_2 ¹⁶ have been found to exhibit enhanced activity compared to those of their pristine compounds. Thus, choosing a suitable dopant is an important criterion toward tuning bond strength, which in turn causes dramatic improvement in the catalytic activity toward HER. Irrespective of superior activity during the initial stage, electrocatalysts are subject to quick activity loss during prolonged cycling, the reasons for which are mainly attributed to catalyst surface poisoning and surface degradation.

The stability of a catalyst, which is arguably the most dominant factor toward commercialization, is often overlooked by the scientific community. Liu et al. reported the synthesis of CoSIP/carbon nanotube (CNT) that shows stability for 2000 cycles.¹⁷ Many other catalysts such as Pt– MoS_x (1000 cycles),² MoPIS (1000 cycles),¹⁸ PdCu@Pd (5000 cycles),¹⁹ NiRu@N-C (1000 cycles),²⁰ N-doped CoS_2 nanowire arrays (3000 cycles),²¹ $\text{Mo}_2\text{C/CNT}$ (1000 cycles),²² $\text{Ni}_3\text{FeN/r-GO}$,²³ structurally deformed MoS_2 (5000 cycles),²⁴ nanoporous CuTi (5000 cycles), Pd-CN_x (10000 cycles),¹ Ni_3S_2 nanosheets array (10000 cycles),²⁵ Ru/CeO_2 (10000 cycles),²⁶ $\text{Co}_9\text{S}_8/\text{NC@MoS}_2$,²⁷ and Mn-CoS_2 (10000 cycles)²⁸ also showed similar stabilities.

In this work, we report the synthesis of Cu-substituted $\text{Pd}_{17}\text{Se}_{15}$ ($(\text{CuPd})_{17}\text{Se}_{15}$) nanoparticles that show enhanced activity, high current density, high turnover frequency (126.3 s^{-1}), and superior stability of 30 000 sweeps toward HER. We tried to address the following scientific points in this work.

- Exact site of substitution by Cu in $\text{Pd}_{17}\text{Se}_{15}$ lattice.* Detailed powder X-ray diffraction (PXRD) analysis together with X-ray absorption spectroscopy (XAS) study revealed the site of substitution.
- The effect of Cu substitution on the structure and oxidation state.* In situ X-ray absorption near-edge spectroscopy (XANES) and DFT calculation analysis revealed the dynamic changes happening on the catalyst surface during electrochemical measurements.
- The driving force for the enhancement of the electrocatalytic activity.* This has been done through a combined experimental and theoretical approach. Unexpected tensile stress induced by the copper substitution and its electronic effect are the key reasons for the enhanced activity and stability compared to those of the pristine compound. Selective copper dissolution further improves the activity generating a very stable catalyst surface for the electrochemical HER that shows stability for 30 000 CV cycles.

We believe that the present study provides a unique way to understand the role of substitution in a lattice at the atomic level and arms us with several degrees of freedom to tune the catalytic activity and stability.

In general, doping/substitution/intercalation of a metal in a compound is clearly reflected by the change in lattice parameters of its unit cell, which completely depends on the size of the substituting metal. This is one of the fundamental ways to design new materials for selected application, and we have exploited a similar strategy in the present work. Copper has a smaller size (atomic radius = 128 pm) compared to that of palladium (atomic radius = 163 pm) or selenium (atomic radius = 190 pm). Thus, the interplanar distance in the $\text{Pd}_{17}\text{Se}_{15}$ lattice is expected to exhibit a decrease with Cu substitution/doping or anisotropic enhancement in the case of intercalation. Since no peaks corresponding to the Cu metal were observed in the

powder XRD pattern (Figure S2), the possibility of intercalation could be easily eliminated. The compound shows reflection profiles consistent with a $Pm\bar{3}m$ crystal space-group symmetry. Profile matching of the experimental powder XRD pattern in Figure 1a,b shows an increase in the lattice parameters of the

Figure 1. Profile matching of the PXRD pattern of (a) $(\text{CuPd})_{17}\text{Se}_{15}$ and (b) pristine $\text{Pd}_{17}\text{Se}_{15}$. Lattice parameters increased from 10.59 Å in pristine $\text{Pd}_{17}\text{Se}_{15}$ to 10.63 Å in $(\text{CuPd})_{17}\text{Se}_{15}$. (c) Simulated PXRD pattern showing the variation in the intensity of PXRD peaks mainly (330) and (331) with variation in Cu substitution. (d) Plot of ratio of intensity of (331):(330) with varying Cu substitution and (e) schematic representation of (330) and (331) crystallographic planes of $(\text{CuPd})_{17}\text{Se}_{15}$.

unit cell, from 10.59 to 10.63 Å after Cu substitution, consistent with the negative shift in PXRD pattern. Thus, contrary to the normal trend (Table S1), it is observed that the interplanar distance in $\text{Pd}_{17}\text{Se}_{15}$ increases upon Cu substitution and the system may apparently be under tensile strain due to Cu substitution. This is further evident from the negative shift of PXRD peak positions (Figure S2). Besides, intensities of a few peaks differ from that of the simulated pattern. To see the influence of Cu substitution on the PXRD pattern, the ATK VNL program suite²⁹ was used to simulate the PXRD pattern of a different percentage of the Cu-substituted $\text{Pd}_{17}\text{Se}_{15}$ lattice and is presented in Figure 1c. (331) and (330) are taken as the representative crystallographic planes due to significant difference upon Cu substitution. A similar trend in the intensity ratio of (331)/(330) was observed in the case of simulated patterns, as illustrated in Figure 1d. Since the intensity of the XRD peak depends upon the scattering and multiplicity factors of a crystal plane, it is expected that the reduction in the peak intensity can be due to the contribution from both. Intensity of the (330) peak decreases with an increase in Cu substitution. These planes have the highest planar density of Pd atom. Hence, they are highly affected by Cu substitution and this changes the mean atomic scattering intensity from the corresponding planes compared to that of its pristine compound. Therefore, the intensity of the peaks with higher planar density of Pd atom

decreases compared to those of the other peaks (as represented by (330) and (331) planes in Figure 1e).

Figure S3a–d shows transmission electron microscopy (TEM) images of the Cu-substituted compound. The *d*-spacing calculated from the high resolution TEM (HRTEM) is 10.65 Å, which corresponds to the (100) crystallographic plane. Selected area electron diffraction presents crowded polycentric rings, which are due to a larger number of atoms within a unit cell (64 atoms), which gives rise to a larger number of diffraction planes. Unsubstituted Pd₁₇Se₁₅ has a Pd atomic percentage of 53.13%, and as seen from energy dispersive analysis X-ray (EDAX) data in Figure S3e, only 15.66% of Cu substitutes Pd, which is nearly one-fourth the total Pd in the system (25% substitution of Pd atoms). Thus, it can be assumed that one-fourth of the Pd atoms are replaced by Cu. Figure S4 shows the core-level XPS spectra of Cu 2p, Pd 3d, and Se 3d. Dividing by the relative sensitivity factor gives a composition of Cu:Pd:Se = 0.37:1.00:1.09.

Hydrogen Evolution Reaction (HER). Electrochemical HER activity of the catalyst has been investigated in 0.5 M H₂SO₄ setup using a three-electrode configuration. After the electrochemical cell was assembled, 80 activation cyclic voltammetry (CV) cycles (at 50 mV/s in the range +0.1 to −0.55 V vs reference hydrogen electrode (RHE)) were run to ascertain that steady state was reached. All the electrochemical measurements were recorded once the steady state was reached. The selective electrochemical dissolution (dealloying) of Cu, during the electrochemical activation procedure, is the key process in the formation of the active catalyst. As shown in Figure 2a, the intensity of the Cu dissolution peak (0.46–0.625 V vs RHE in the forward scan) decreases gradually with the increasing number of potential cycles, indicating Cu dissolution from (CuPd)₁₇Se₁₅ NPs. Activity of the catalyst increases upon Cu dissolution, as shown in Figure 2b. All the electrochemistry from now on has been recorded on the dealloyed catalyst.

Figure 2b shows the polarization curve of the catalyst before and after the activation process with a consecutive interval of 20 cycles. The onset potential of the catalyst decreases by 60 mV after 80 cycles of activation. The onset potential was calculated as the potential required to reach 0.1 mA cm^{−2} current density, which is found to be around 85.4 mV, which decreased to 76.1 mV after 10 000 cycles and remained stable thereafter. A current density of 10 mA cm^{−2} was achieved at an overpotential of 188.5 mV. Figure 2c shows the positive shift of the onset potential of Pd₁₇Se₁₅ after Cu substitution.

Dealloyed (CuPd)₁₇Se₁₅ shows a Tafel slope value of 48 mV dec^{−1}, which is close to that of Pt/C (29 mV dec^{−1}) and much improved from the pristine Pd₁₇Se₁₅ (71.2 mV dec^{−1}) and (CuPd)₁₇Se₁₅ (52 mV dec^{−1}) values under identical reaction conditions.

Hence, the value of the Tafel slope clearly indicates that HER on the dealloyed catalyst follows the Volmer–Heyrovsky mechanism, with electrochemical desorption of hydrogen as the rate-limiting step.³⁰ Impedance spectroscopic data show the charge-transfer resistance for the Cu-substituted catalysts (58.8 Ω) to be less than half of the R_{ct} value (179.6 Ω) for the pristine compound (Figure 2e), confirming that faster charge-transfer kinetics for the Cu-substituted compound is beneficial for the efficient charge transfer, which is in good agreement with the low Tafel slopes.

The TOF is the ideal figure of merit to correlate the intrinsic activities of different catalyst materials. The TOF for the substituted compound reaches 0.19, 2.05, and 126.3 s^{−1} at overpotentials of 0, 100, and 200 mV, respectively, which is

Figure 2. (a) Cyclic voltammogram recorded at a scan rate of 0.05 V/s in 0.5 M H₂SO₄ showing the oxidative removal of Cu from the system during the activation cycles. A steady state was achieved after 80 cycles. (b) Polarization curve showing the activation of the catalyst after every 20 cycles until stable curve is achieved. (c) Comparison of linear sweep voltammetry (LSV) plots showing positive shift in the onset potential for (CuPd)₁₇Se₁₅ compared to Pd₁₇Se₁₅. (d) Comparison of the Tafel slopes of the catalyst before and after the accelerated degradation test. (e) Electrochemical impedance spectra (EIS) showing the decrease in charge-transfer resistance of the Cu-substituted catalyst. (f) Time of flight (TOF) value of Pd₁₇Se₁₅ and (CuPd)₁₇Se₁₅ showing improvement in the catalytic behavior after Cu substitution.

several times higher than that in the pristine Pd₁₇Se₁₅ (Figure 2f). The TOF for the carbon support was calculated and found to be too low to have any appreciable effect on the TOF of the compound and hence it is neglected. Comparison of the TOF value with that the Pd₁₇Se₁₅ is presented in Table S2. The TOF calculated for the dealloyed (CuPd)₁₇Se₁₅ is much higher than those for previously reported compounds such as Au (0.3 s^{−1} @ 200 mV),³¹ AuNi (0.0334 s^{−1} @ 80 mV),³² Ni₂P (0.015 s^{−1} @ 100 mV),³³ P/Se-MoS₂/CFP (0.4 s^{−1} @ 150 mV),³⁴ CoPS (3.38 s^{−1} @ 100 mV),³⁵ Ru/MeOH/THF (0.87 s^{−1} @ 100 mV),³⁶ and Ni–C–N (6.67 @ 200 mV).³⁷

Structural Changes upon Cu Substitution. Better activity of the Cu-substituted compound can be envisaged by simulating the coordination environment around Se. Density functional theory (DFT) calculation was used to relax the cell parameters of the unit cell after 25% substitution of Pd atoms with Cu in the unit cell. Se in Pd₁₇Se₁₅ is found to exist in three different coordination environments: one tetrahedral and two distorted square pyramidal. Figure S5 shows the coordination environment around Se before and after Cu substitution.

It must be noted that after structural optimization, Cu–Se has a smaller bond length compared to Pd–Se bonds. The decrease in the Cu–Se bond length (2.4120–2.4480 Å in the tetrahedral arrangement and 2.4860–2.5160 Å in square pyramidal arrangement), compared to the Pd–Se bond length, is because

Figure 3. (a) X-ray absorption near edge spectroscopy of Se K-edge of Se foil, $\text{Pd}_{17}\text{Se}_{15}$, $(\text{CuPd})_{17}\text{Se}_{15}$, CoSe, and NiSe. Comparison of changes in white-line intensity gives a relative idea about the change in oxidation state of Se in various compounds ranging from 0 oxidation state in Se foil to -2 oxidation state in CoSe and NiSe. (b) Fourier transformed R-space data showing the appearance of a Se–Cu peak at a lower radial distance and a Se–Pd peak at a higher radial distance than for the pristine compound and schematic showing the effect of copper substitution in the $\text{Pd}_{17}\text{Se}_{15}$ lattice. In situ XANES spectra of $(\text{CuPd})_{17}\text{Se}_{15}$ showing change in the oxidation state happening to the constituent elements. (c) Unnormalized Cu K-edge XANES spectra showing the chemical dissolution of Cu. (d) Normalized Cu K-edge XANES spectra showing the shift in edge energy during the electrochemical process. (e) Se K-edge XANES spectra showing the variation in oxidation state of the Se. (f) Ex situ Pd K-edge XANES spectra showing the intermediate oxidation state of Pd in $(\text{CuPd})_{17}\text{Se}_{15}$.

of the increase in charge transfer from Cu to Se owing to substantial electronegativity difference between the two. Henceforth, the increase in the electron density around Se decreases the effective nuclear charge exerted by the nucleus, thereby increasing the Pd–Se bond distance (from 2.4930 to 2.5770 Å to 2.5110–2.5770 Å after Cu substitution as seen from DFT calculation). Figure S6 shows the domino effect of elongation of Pd–Se bond length that traverses along the Pd–Se chain length to finally increase the edge length of the unit cell. Therefore, the system experiences tensile stress. This corroborates well with the increase in cell parameters obtained from profile matching of the PXRD pattern.

Change in Oxidation State upon Copper Substitution. The white-line intensity in the Se K-edge XANES pattern corresponds to the $1s \rightarrow 4p$ electronic transition. The higher the number of electrons in the p-orbital (higher the negative oxidation state), the lower is the white-line intensity. Figure 3a indicates that the Se foil has the highest white-line intensity followed by $\text{Pd}_{17}\text{Se}_{15}$ and $(\text{CuPd})_{17}\text{Se}_{15}$. NiSe and CoSe listed in Figure 3a have -2 oxidation states and are used as references for determining the oxidation state in $(\text{CuPd})_{17}\text{Se}_{15}$. Thus, it is reasonable to anticipate that Se in $(\text{CuPd})_{17}\text{Se}_{15}$ has a higher negative oxidation state compared to that in pristine $\text{Pd}_{17}\text{Se}_{15}$. This indicates the increase in charge transfer from Cu to Se, which is possible only when Cu and Se are close to each other and is also confirmed from the theoretical calculation. This, sequentially, decreases the effective nuclear charge around Se. Thus, the Pd–Se bond distance increases, which is evident from the radial distribution function of EXAFS spectra shown in Figure 3b. $\text{Pd}_{17}\text{Se}_{15}$ has a single peak in R-space that splits to two peaks in the case of $(\text{CuPd})_{17}\text{Se}_{15}$, one having a lower and another a higher bond distance corresponding to Se–Cu and Se–Pd bond distances, respectively. This is evident from the structural parameters obtained from the fitted first coordination shell (Table S3). The Pd–Se scattering path increase in distance (from its ideal position of 2.433 Å to 2.458 Å), while the Se–Cu

scattering path decreases in bond distance (from its ideal position of 2.118 Å to 1.951 Å) (Figure S7).

In order to investigate the chemical changes during the dealloying process, in situ XAS study of the compound was performed. Figure 3c shows the unnormalized Cu K-edge XANES pattern of the compound before and after electrochemical measurements. A decrease in the edge jump of the spectra, when Cu is dipped in 0.5 M H_2SO_4 solution, is attributed to the dissolution of Cu(II) in the acidic electrolyte, thus reducing the amount of Cu in the sample. Comparing the energies (E_0) in the normalized Cu K-edge XANES spectra (Figure 3d), we find that Cu in the compound before the electrochemical treatment exhibits both $+1$ and $+2$ oxidation states. When dipped into the acidic electrolyte, Cu(II) dissolves into the acidic electrolyte, leaving behind Cu in predominantly the $+1$ oxidation state in the catalyst. This is clearly detected in the shoulder peak, observed in the XANES pattern, attributed to $1s \rightarrow 4p_z$ transition.³⁸ The peak becomes predominant after the dealloying process. Se K-edge XANES spectra of the compound show that when Cu is dipped in acidic electrolyte, the white-line intensity increases and reaches the same height as in pristine $\text{Pd}_{17}\text{Se}_{15}$, indicating Se is in the same oxidation state as in $\text{Pd}_{17}\text{Se}_{15}$ (as shown in Figure 3e). The comparison of Pd K-edge XANES spectra of Pd foil, pristine $\text{Pd}_{17}\text{Se}_{15}$, and $(\text{CuPd})_{17}\text{Se}_{15}$ (Figure 3f) reveals an intermediate oxidation state between 0 and $+2$ for Pd in $(\text{CuPd})_{17}\text{Se}_{15}$.

In addition to electronic effects, the morphological effect such as increase in surface area, electrochemically active surface area (ECSA) in this case, may also contribute to the enhanced activity due to Cu substitution. The assessment of the ECSA of the samples was carried out by running cyclic voltammetry (CV) measurements at various scan rates (20, 40, 60, 80, and 100 mV s^{-1}) in the nonfaradaic region 0.03–0.23 V vs RHE where the current response is mostly due to the charging of the double layer. The double-layer capacitance was calculated by plotting

Figure 4. (a) Linear sweep voltammogram of the Cu-substituted catalyst showing prolonged stability of the catalyst even after 30 000 cycles and (b) comparison of the Tafel slopes of the catalyst before and after the degradation test. (c) Schematic representation of different possible sites of Cu substitution and (d) comparison of the changes in Gibbs free energy of adsorption of H^* before and after Cu substitution.

the $\frac{1}{2}\Delta J$, i.e., $\frac{1}{2}(J_a - J_c)$, where J_a and J_c are cathodic and anodic current, respectively, at 0.15 V vs RHE against the scan rate (Figure S8).³⁹ It is well-known that C_{dl} is directly proportional to the ECSA. Hence, a lower value of C_{dl} for the Cu-substituted compound (0.336 mF cm^{-2}) compared to that of the pristine compound (0.498 mF cm^{-2}) suggests that enhancement in the activity of the substituted compound is purely due to the electronic effect that resulted from the tensile stress and electronic effect in the system imposed by the Cu atoms.

Electrochemical Stability. Performance stability tests of a dealloyed $(\text{CuPd})_{17}\text{Se}_{15}$ catalyst was checked for 30 000 potential cycles (Figure 4a), between 0 and -0.4 V vs RHE, with no change in the activity of the catalyst exhibiting ultrahigh stability for a prolonged time. This Tafel slope of the catalyst has been increased from 48 mV dec^{-1} , in the dealloyed catalyst, to 62 mV dec^{-1} after the degradation test, as illustrated in Figure 4b.

The commercial application of any catalyst can be extended if it can be used over a wide pH range. In this direction, the activity of the catalyst was also checked in an alkaline electrolyte of 0.5 M KOH . Interestingly, the catalyst was found to show a current density of 10 mA cm^{-2} at an overpotential of 375 mV , which remains almost the same even after 30 000 cycles. Slight negative shift in the polarization curve shown in Figure S9 shows the high stability of the catalyst even in alkaline medium. Faradaic efficiency in the case of $(\text{CuPd})_{17}\text{Se}_{15}$ is calculated to be close to 100% and shown in Figures S10 and S11.

Theoretical Calculation. DFT calculation was executed through substitution of equivalent sites of Pd with Cu. Since there are four types of Pd in the lattice, substitution in the four equivalent sites is possible. But we neglected one of the site as it contributes to more than 25% of substitution of Pd. Thus, we end up with three different possibilities of Cu substitution, namely, CuA, CuB, and CuC, as represented in Figure 4c. In all the cases, the lattice parameter of the unit cell increased after Cu

substitution from $10.606 \text{ \AA}$ ($\text{Pd}_{17}\text{Se}_{15}$) to $10.6904 \text{ \AA}$ (CuA), $10.7155 \text{ \AA}$ (CuB), and $10.7156 \text{ \AA}$ (CuC). Cu leaching further increased the lattice parameter, as shown in Table S4. According to Nørskov,³ an increase in the lattice parameter shifts the d -band center toward the Fermi level. This results in a decrease in the occupation of antibonding orbitals and hence a stronger metal–adsorbate bond. This is reflected by the ΔG_H adsorption calculation, which is presented in Figure 4d. It is clearly observed that the number of active sites having optimal adsorption has increased after the Cu substitution. Due to d -band center shift toward the Fermi level, Se–H bonds get stronger and Se starts acting as the active site. Only few of the Pd sites have an optimal adsorption toward H^* . Unlike in $\text{Pd}_{17}\text{Se}_{15}$, Pd in $(\text{CuPd})_{17}\text{Se}_{15}$ has an intermediate oxidation state between 0 and +2, as observed from Pd K-edge XANES data; hence, it weakly adsorbs H^* . This indicates that a few of the Pd sites are activated after Cu substitution. To justify that Pd is not mainly the active sites, Pd sites were blocked electrochemically by CO adsorption and the activity was tested as shown in Figure S12a,b. A slight left shift in the onset potential was observed as only few Pd sites were active and got blocked. The remarks made in this work further explain the observation made by Kukuluri et al.⁴⁰ They observed a considerable amount of Se DOS contribution near the Fermi level. In addition, the hydrogen adsorption/desorption peaks, as observed for Pd/Pt-based compounds were not observed for this compound. This supports the fact that only few Pd and mainly Se act as the active sites for the HER. Since Se mainly acts as the active site, the d -band model proposed by Hammer and Nørskov³ was applied and strain and ligand effects were deconvoluted on these sites and presented in Figure 5.^{41,42} Se^{II} in CuA, Se^{III} in CuB, and Se^{I} in CuC are directly connected to Cu in the doped system. Hence, they exhibit the highest ligand effect. Se atoms further away from the Cu remain unaffected from the ligand effect. They experience only the strain effect. Se^{I} in CuA, Se^{I} in CuB, and Se^{III} in CuC have their

Figure 5. Deconvolution of strain, ligand and ensemble effect on Se sites of $(\text{CuPd})_{17}\text{Se}_{15}$. S, L, and E in the figure represents strain, ligand, and ensemble effect, respectively. Se^{I} , Se^{II} , and Se^{III} represents different sites of Se.

sole contributions only from strain effect. Hirshfeld charge analysis of the system before and after Cu substitution is presented in Table S5. It can clearly be seen that the sites having contributions from both ligand and strain effects have ΔG_{H} close to 0 and hence show better activity.

In conclusion, we highlighted an in-depth understanding of the atomic strain engineering in the system through the introduction of a smaller atom with the assistance of both experimental and theoretical studies. Cu substitution in $\text{Pd}_{17}\text{Se}_{15}$ system imposes tensile stress to the system, which then enhances the activity of the system through modulation of the electronic structure. These nanoparticles are highly stable during 30 000 cycles of accelerated degradation testing and have recorded TOF value of 126.3 s^{-1} at an overpotential of 200 mV. These studies can potentially impact designing many new catalysts for HER and/or other electrochemical studies by atomic strain engineering through appropriate chemical substitution. A detailed understanding of this compound will help in designing and redefining our concepts of strain engineering to enhance the activity of such catalysts.

■ ASSOCIATED CONTENT

Supporting Information

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Characterization, experimental details, XRD, EDAX, XPS, electrochemical performance results, additional experiment results, DFT calculations (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*S. C. Peter. E-mail: sebastiancp@jncasr.ac.in.

ORCID

Saurav Ch. Sarma: 0000-0002-6941-9702

Vidyanshu Mishra: 0000-0002-8660-2859

Sebastian C. Peter: 0000-0002-5211-446X

Notes

The authors declare no competing financial interest.

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