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Complete List of Authors:	Liu, Fanghan; Huazhong University of Science and Technology, School of Energy and Power Engineering Liu, Cong; Argonne National Laboratory, Chemical Sciences and Engineering Division Zhong, Xiaoliang; Huazhong University of Science and Technology, School of Energy and Power Engineering; Huazhong University of Science and Technology, School of Energy and Power Engineering

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## COMMUNICATION

## Enhancing Electrocatalysis for Hydrogen Production over CoP Catalyst by Strain: a Density Functional Theory Study

Fanghan Liu<sup>a</sup>, Cong Liu<sup>b</sup> and Xiaoliang Zhong<sup>\*ac</sup>Received 00th January 20xx,  
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**Facet-dependent strain effects on hydrogen evolution reaction catalyzed by CoP are studied based on density functional theory methods. We show that both atomic and electronic effects need to be taken into consideration to understand the strain effects. For (111) surface tensile strain promotes hydrogen evolution at all hydrogen coverages. For (101) surface a moderate tensile strain of ~3% turns this facet to optimum performance.**

The production of hydrogen fuel by economic water splitting methods provides an intriguing route towards sustainable clean energy<sup>1</sup>. However, the hydrogen evolution reaction (HER) is mostly catalysed by Pt, a rare and expensive element, which impedes its massive utilization. Recently, transition metal phosphides (TMPs) have been intensively investigated to replace platinum, which show active catalytic properties for HER<sup>2</sup>. Among the studied TMPs, CoP is especially promising due to its high performance, high stability and facile fabrication<sup>2-6</sup>.

Although being an active HER catalyst, performance of CoP is still significantly lower than that of Pt<sup>2</sup>. Recent research efforts have established the strength of strain engineering in optimizing electrocatalytic properties of noble-metal-based catalysts<sup>7</sup>. Although TMPs are very promising HER catalysts, we note that strain effects on TMPs have rarely been studied. In the present work we study the possibility of utilizing surface straining to improve CoP performance towards more practical Pt replacement. In fact, fine tuning of surface strain towards catalyst optimization is under active research via, for example, core-shell structuring<sup>7</sup>, in situ transformation<sup>8</sup> and substrate-catalyst interaction<sup>9</sup>. Interestingly, cobalt (II) oxide (CoO), which

was traditionally considered as HER-inactive, became highly active for HER when a tensile strain is applied to its surface<sup>10</sup>. In another work, nickel phosphide (NiP) showed an increased turnover frequency of 24 times for HER when a substantial compressive strain of 5.6% is induced<sup>8</sup>. We expect our contribution could serve as the solid theoretical guidance for experimental investigations to utilize strain effect to promote hydrogen evolution on CoP.

Rational improvement in catalysts performance requires solid understanding of catalysis mechanism. The high activity of TMPs has recently been correlated with the small hydrogen adsorption free energy ( $\Delta G_H$ )<sup>2</sup>. The as-synthesized CoP nanostructures are typically multi-faceted, with more than one crystal facets exposed which may function as the active sites<sup>4-6</sup>. As such, identifying the active surfaces is crucial. Density functional theory (DFT) methods<sup>11, 12</sup> have shed light by calculating  $\Delta G_H$  on CoP. It is found that TMPs follow the Sabatier principle, that is, materials with optimum performance exhibit close to zero  $\Delta G_H$ <sup>2, 13</sup>. Kibsgaard et al. studied a series of TMPs and indicated that high performance of CoP originated from the (101) surface<sup>2</sup>. For this surface, DFT calculations assigned a small  $\Delta G_H$  of -0.085 eV, explaining the high performance. Hu et al. looked into hydrogen adsorption on various low-Miller-index surfaces of CoP via DFT calculations<sup>14</sup>. They concluded that (111) surface of CoP is thermodynamically stable with  $\Delta G_H$  smaller than 0.1 eV in magnitude. Notably, most of the recent studies on CoP assigned the active facets to either the (101)<sup>15-18</sup> or (111)<sup>19, 20</sup> surface.

As shown in Figure 1, the CoP crystal has an orthorhombic unit cell. The present DFT study will focus on strain effects on both (111) and (101) surfaces. As mentioned above, these two are identified as the active facets for HER. Besides (111) and (101) surfaces, we have also calculated strain effects on other facets ((110), (100), and (011)) which were studied in reference<sup>14</sup>. The results are summarized from Fig. s2 to Fig. s4 in the Supporting Information. The detailed analysis for these facets is, however, beyond the scope of this work. For the (111) surface, previous study shows that hydrogen adsorption highly

<sup>a</sup> Department of New Energy Science and Engineering, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China. E-mail: [xzhong@hust.edu.cn](mailto:xzhong@hust.edu.cn)

<sup>b</sup> Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA

<sup>c</sup> State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

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depends on coverage rate<sup>14</sup>. For low hydrogen coverage ( $\leq 25\%$ ),  $\Delta G_H$  is as low as  $-0.6$  eV indicating too strong adsorption. For higher coverage ( $>25\%$ ), magnitude of  $\Delta G_H$  is around  $0.1$  eV, signalling good HER catalysis. Our model is similar to the reported one<sup>14</sup>. The adsorption of 1, 2, 3 and 4 hydrogen atoms to a simulation unit surface (Fig. 1) corresponds to an H coverage of 25%, 50%, 75% and 100%, respectively.

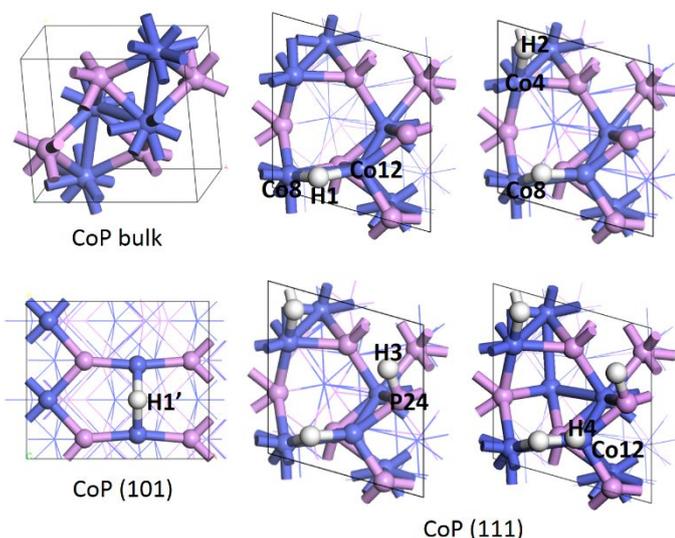


Fig. 1 Optimized structures of CoP bulk crystal as well as (111) and (101) surfaces at different H coverages. H1, H2, H3 and H4 represents hydrogen coverage of 25%, 50%, 75% and 100% on the (111) surface, respectively. H1' represents hydrogen coverage of 25% on the (101) surface. Colour scheme: H in grey, Co in blue and P in purple.

The first H atom (H1) binds with 2 Co atoms (Co8 and Co12) at the bridge site (Figure 1), exhibiting lowest  $\Delta G_H$  among different adsorption sites on the (111) surface. After the adsorption of the first atom, the second H atom (H2) also binds with 2 Co atoms (Co4 and Co8) at the bridge site. Then the third H atom (H3) binds to 1 P atom (P24). Finally, the fourth H atom (H4) binds to 1 Co atom (Co12). The present results are in good agreement with the reported<sup>14</sup>, i.e., while H1 exhibits a low  $\Delta G_H$  of  $-0.53$  eV (without consideration of strain), H2 to H4 show  $\Delta G_H$  with magnitude no greater than  $0.2$  eV (Fig. 2).

In reference<sup>14</sup>, the authors used a  $2 \times 2$  supercell model for the (111) surface. In our calculation, we use a  $1 \times 1$  unit cell model. We would like to point out that, although there is difference between our model and reference<sup>14</sup>, the calculated  $\Delta G_H$  in general agrees well with reference<sup>14</sup>. As shown in Fig. 2, our calculation yields  $\Delta G_H$  of  $-0.53$ ,  $0.01$ ,  $-0.04$  and  $0.14$  eV at coverage of 25%, 50%, 75% and 100% on the (111) surface, respectively. From Fig. 4 in reference<sup>14</sup> one finds  $\Delta G_H$  of  $-0.6$ ,  $-0.1$ ,  $-0.1$  and  $0.1$  eV at these coverages. Thus, although our model is smaller, we get  $\Delta G_H$  in line with reference<sup>14</sup>.

For CoP (101) surface we consider only one H atom adsorbed at Co bridge site to the surface unit cell (Fig. 1), which corresponds to an H coverage of 25%. This is the steady-state and most active H coverage<sup>2</sup>. Since CoP (101) surface is likely to operate at this low hydrogen coverage rate, higher H coverage rate is expected to be irrelevant to HER<sup>2</sup>.

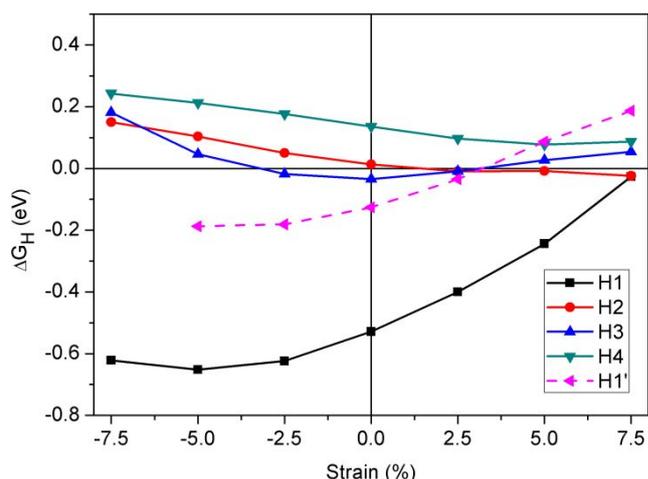


Fig. 2 Evolution of CoP surface hydrogen adsorption free energy as a function of applied strain. H1 to H4 corresponds to hydrogen on the (111) surface, while H1' corresponds to hydrogen on the (101) surface (see Fig. 1).

Figure 2 presents the variation of  $\Delta G_H$  when strain is applied to CoP surfaces, showing interesting features. With low H coverage of 25% (H1 and H1'),  $\Delta G_H$  increases (more positive) with expansive strains on both the (111) and (101) surfaces. For H1 on (111) surface,  $\Delta G_H$  spans a considerable energy range of about  $0.6$  eV in the considered strain range (from  $-7.5\%$  to  $7.5\%$ ). Notably,  $\Delta G_H$  is calculated to be  $-0.03$  eV when a tensile strain (positive strain) of  $7.5\%$  is applied, signalling HER performance is close to optimum for this adsorption site ( $\Delta G_H$  equals to zero). It is to be noted that without applying strain, H1 adsorption site is not expected to be HER-active due to low  $\Delta G_H$ <sup>14</sup>. When a compressive strain (negative strain) is applied,  $\Delta G_H$  is even lower than the value at zero strain ( $-0.53$  eV), indicating worse catalytic properties for this site. For H1' on (101) surface, unstained  $\Delta G_H$  of  $-0.13$  eV is also close to the reported ( $-0.09$  eV<sup>2</sup>). Figure 2 indicates a positive strain of about  $+3\%$  turns H adsorption to the energy-neutral point, i.e.,  $\Delta G_H$  equals to zero. This is very interesting since HER rate is proportional to the exponential of  $\Delta G_H^2$ , such that decrease of  $\Delta G_H$  (in magnitude) indicates a notable promotion of HER. On the other hand, compressive strain renders more negative  $\Delta G_H$  which negatively affects hydrogen evolution.

On the other hand, for higher H coverages (H2 to H4) on (111) surface,  $\Delta G_H$  shows significantly less variation of about  $0.2$  eV in the whole strain range. For H2 and H4, the variation of  $\Delta G_H$  is monotonic with applied strain and decreases when surface is expanded. For H3, a lowest  $\Delta G_H$  appears around zero strain and either tensile or compressive strain shifts up  $\Delta G_H$ . Interestingly, at tensile strain of about  $7.5\%$  all H coverages from H1 to H4 exhibit  $\Delta G_H$  smaller than  $0.1$  eV in magnitude. This implies considerably improved HER catalysis with all hydrogen adsorption sites close to highest performance.

We note that both the atomic and electronic effects need to be taken into account, to explain the change of hydrogen adsorption strength under strain. Atomically, H atoms adsorbed at Co bridge sites (H1, H2 and H1') undergo H-Co bond length change on surface straining (Table 1). These H atoms bind with 2 Co atoms. When the 2 Co atoms get apart/closer as a result of

strain applying, the corresponding H-Co bond length increases/decreases. To better understand the trend of  $\Delta G_H$  variation as shown in Fig. 2, we plot in Fig. 3(a) the percentage change of bond length between adsorbed hydrogen and CoP surface atoms (either Co or P, Table 1) with which hydrogen bind.

Table 1. Bond length in Å at H adsorption under strain for both (111) and (101) surfaces. H1 to H4 are hydrogen atoms on (111) while H1' is on (101).

Strain		-5%	0	+5%
Bond length	H1(Co8, Co12)	1.643, 1.641	1.674, 1.682	1.709, 1.740
	H2(Co4, Co8)	1.646, 1.622	1.646, 1.639	1.663, 1.658
	H3(P24)	1.456	1.448	1.444
	H4(Co12)	1.481	1.480	1.480
	H1'(Co12', Co24')	1.684	1.720	1.754

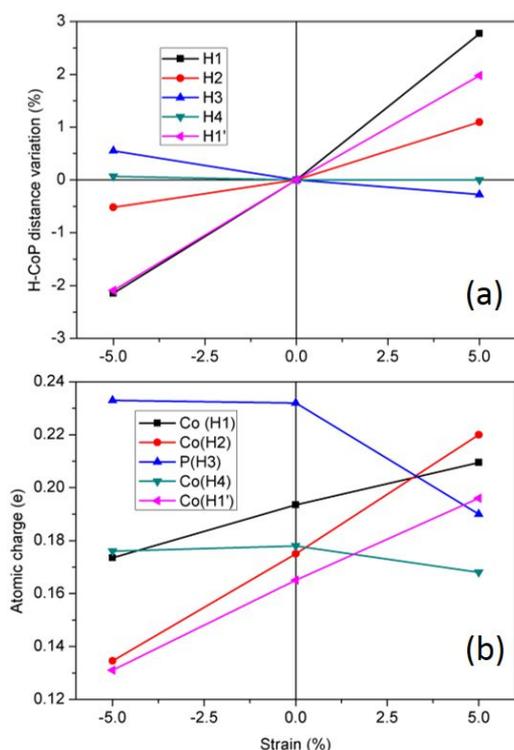


Fig 3. (a) Percentage change of H-CoP surface bond length at -5%, 0 and +5% strain (see text). (b) Atomic charge variation of CoP surface atoms with hydrogen adsorption under strain. The corresponding adsorbed hydrogen atoms are shown in parentheses.

As expected, hydrogen adsorbed at Co bridge sites (H1, H2 and H1') has the largest variation of bond length under strain (Fig. 3. (a)). On the other hand, for H3 and H4 on the (111) surface, these H atoms only form chemical bonds with 1 surface atom, with much less change of bond length between H and surface atoms under strain (Fig. 3(a)). One would expect decreased H binding strength for increased H-Co bond lengths. This is indeed the case for H1 and H1', for which the corresponding H-Co bond lengths are significantly affected by strain (Fig. 3(a)). These H atoms exhibit increased  $\Delta G_H$  at expansive strain (Fig. 2). However, although H-Co bond lengths for H2 also increase

when surface expands (Fig. 3(a)),  $\Delta G_H$  decreases for positive strains (Fig. 2). Thus, atomic effects alone are not able to cover the strain effects on hydrogen adsorption for all hydrogen coverages.

Electronically, surface straining also leads to variation of surface Co-P bond lengths, which in turn, results in variation of charge transfer between Co and P atoms. As Fig. 3(b) shows, Co atoms (Co4 and Co8) at H2 adsorption are most prone to applied strain. The (averaged) Co atom charge increases by almost 0.1 e from -5% to +5% strain. This indicates Co4 and Co8 become significantly more positively charged on surface expansion. Compared with H1 and H1', H-Co bond lengths of H2 changes less under strain (Fig. 3(a)). On the other hand, Co atom charge at H2 adsorption changes more under strain (Fig. 3(b)). Consequently, the electronic effects surpass the atomic effects for H2. Under expansive strain, more positively charged Co4 and Co8 interact with adsorbed H2 more strongly, leading to decreased  $\Delta G_H$  (Fig. 2). For H3 and H4, both the atomic effects (Fig. 3(a)) and electronic effects (Fig. 3(b)) are in general small, leading to small change of  $\Delta G_H$  under strain (Fig. 2).

The d-band model has been widely used to understand strain effects on noble-metal-based catalysts, where the variation of  $\Delta G_H$  is correlated with the shift of the center of metal d bands<sup>15</sup>. To compare with strain effects on metal, we have studied electronic structure of CoP (111) surface under strain denoted by the d-band projected density of states (PDOS) of the adsorption sites (Fig. 3). For both H1 and H2, d-band PDOS appears to shift up when surface is expanded (more positive strain). Quantitatively, d-band centre for H1 adsorption site is calculated to be -2.28, -2.16 and -2.03 eV at a strain of -5%, 0 and +5%, respectively. For H2 adsorption site, d-band centre is -2.54, -2.42 and -2.26 eV at these strains. Comparing Fig. 3 (b) and Fig. 4 one notes that charge transfer between Co and P determines the location of d-band center. At positive strain, Co atoms become more positively charged. The reduction of electron occupation causes a up-shift of d-band (Fig. 4). However, the d-band center model only manifests the electronic effects. As discussed above, the atomic effects may surpass the electronic effects. As such, the d-band center model can't be used alone to explain the strain effects.

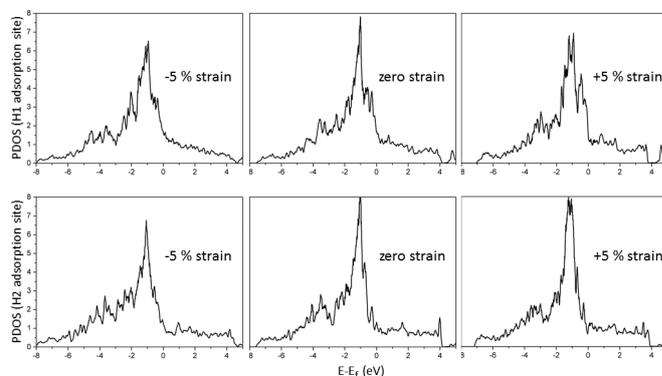


Fig. 4 Evolution of d-band PDOS (arbitrary unit) under strain for both H1 adsorption site (Co8 and Co12, the upper part) and H2 adsorption site (Co4 and Co8, the lower part) of CoP (111) surface.

In summary, we have investigated the possibility of enhancing hydrogen evolution over CoP by means of surface straining. CoP is intrinsically highly active for HER as a result of the small  $\Delta G_H$ . Based on DFT calculations we show that applying surface strain is very promising to further improve CoP's catalytic properties by tuning  $\Delta G_H$ . For both the already active (111) and (101) surfaces, tensile strain appears to bring  $\Delta G_H$  even closer to zero. Especially, for the (101) surface a moderate tensile strain of about 3% is predicted to render a zero  $\Delta G_H$ . We disclose that both atomic variation and electronic variation affect  $\Delta G_H$  under strain. For H1 on (111) surface and H1' on (101) surface, variation of hydrogen adsorption energy is majorly caused by enlarged Co-Co bond lengths under tensile strain, which in turn results in an increase of H-Co bond lengths. For H2 on (111) surface, the electronic effects surpass the atomic effects. The interplay between atomic and electronic effects yields complex variation of  $\Delta G_H$  under strain, for different hydrogen coverages as shown in Fig. 2. It is to be noted that the details of DFT calculation such as unit cell size and used functional may slightly change calculated value of  $\Delta G_H$ . However, we think the disclosed trend in  $\Delta G_H$  variation under strain should be robust, as we have disclosed the atomic and electronic origins for  $\Delta G_H$  changes. Considering the active research efforts being conducted for catalysts strain engineering and the recent success on CoO<sup>10</sup> and NiP<sup>8</sup>, we expect the present work to serve as a solid theoretical guidance for future experimental strain manipulation on CoP.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references

- W. Lubitz and W. Tumas, *Chemical Reviews*, 2007, **107**, 3900-3903.
- J. Kibsgaard, C. Tsai, K. Chan, J. D. Benck, J. K. Nørskov, F. Abild-Pedersen and T. F. Jaramillo, *Energy & Environmental Science*, 2015, **8**, 3022-3029.
- T. Liu, L. Xie, J. Yang, R. Kong, G. Du, A. M. Asiri, X. Sun and L. Chen, *ChemElectroChem*, 2017, **4**, 1840-1845.
- X. Q. Ji, R. Zhang, X. F. Shi, A. M. Asiri, B. Z. Zheng and X. P. Sun, *Nanoscale*, 2018, **10**, 7941-7945.
- E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, *Angewandte Chemie-International Edition*, 2014, **53**, 5427-5430.
- J. Tian, Q. Liu, A. M. Asiri and X. Sun, *Journal of the American Chemical Society*, 2014, **136**, 7587-7590.
- M. Luo and S. Guo, *Nature Reviews Materials*, 2017, **2**, 17059.
- J. Duan, S. Chen and C. Zhao, *ACS Applied Materials & Interfaces*, 2018, **10**, 30029-30034.
- T. Nilsson Pingel, M. Jørgensen, A. B. Yankovich, H. Grönbeck and E. Olsson, *Nature Communications*, 2018, **9**, 2722.
- T. Ling, D.-Y. Yan, H. Wang, Y. Jiao, Z. Hu, Y. Zheng, L. Zheng, J. Mao, H. Liu and X.-W. Du, *Nature Communications*, 2017, **8**, 1509.
- P. Hohenberg and W. Kohn, *Physical Review*, 1964, **136**, B864-B871.
- W. Kohn and L. J. Sham, *Physical Review*, 1965, **140**, A1133-A1138.
- J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *Journal of The Electrochemical Society*, 2005, **152**, J23-J26.
- G. Hu, Q. Tang and D.-e. Jiang, *Physical Chemistry Chemical Physics*, 2016, **18**, 23864-23871.
- R. Zhang, C. Tang, R. Kong, G. Du, A. M. Asiri, L. Chen and X. Sun, *Nanoscale*, 2017, **9**, 4793-4800.
- T. T. Liu, X. Ma, D. N. Liu, S. Hao, G. Du, Y. J. Ma, A. M. Asiri, X. P. Sun and L. Chen, *Acs Catalysis*, 2017, **7**, 98-102.
- T. T. Liu, D. N. Liu, F. L. Qu, D. X. Wang, L. Zhang, R. X. Ge, S. Hao, Y. J. Ma, G. Du, A. M. Asiri, L. Chen and X. P. Sun, *Advanced Energy Materials*, 2017, **7**.
- Q. Zhou, Z. Shen, C. Zhu, J. Li, Z. Ding, P. Wang, F. Pan, Z. Zhang, H. Ma, S. Wang and H. Zhang, *Advanced Materials*, 2018, **30**, 1800140.
- C. Guan, W. Xiao, H. Wu, X. Liu, W. Zang, H. Zhang, J. Ding, Y. P. Feng, S. J. Pennycook and J. Wang, *Nano Energy*, 2018, **48**, 73-80.
- S. H. Yu and D. H. C. Chua, *ACS Applied Materials & Interfaces*, 2018, **10**, 14777-14785.