Study on oxygen reduction mechanism of S-doped Fe-NC monatomic catalyst
Xiaoqing Lu*, Shoufu Cao, Xiaofei Wei, Shaoren Li, Shuxian Wei
School of Materials Science and Engineering, China University of Petroleum, Qingdao 266580, Shandong Province, China. E-mail: luxq@upc.edu.cn

ABSTRACT
Heteroatom doped Fe-NC catalyst shows excellent performance in oxygen reduction reaction. In this work, density functional theory was used to study the mechanism of S atom doping on the regulation of electronic structure of Fe-NC monatomic catalyst and the promotion of oxygen reduction reaction. The stable configuration of Fe-NC catalyst after sulfur atom doping, the regulation of electronic structure of fen4 active site by S atom, and the mechanism of oxygen adsorption and oxygen reduction reaction were analyzed. The results show that doping a small amount of S atoms around the fen4 active site can improve the stability of the catalyst. The mechanism of S atom doping to improve oxygen reduction performance is as follows: (1) the doping of S atom reduces the band gap of the catalyst, improves the conductivity of the catalyst, and is conducive to the electrocatalytic oxygen reduction reaction; (2) the doping of S atom can improve the ability of the catalyst to adsorb oxygen, which is conducive to oxygen reduction reaction; (3) the introduction of four S atoms into the system can reduce the overpotential of oxygen reduction reaction and improve the catalytic activity of fen4 site for oxygen reduction reaction. This work may provide a new idea for the regulation of heteroatom doping on carbon-based monatomic catalysts.

Keywords: Fe-NC Catalyst; Heteroatom Doping; Oxygen Reduction Reaction; Density Functional Theory

1. Introduction
The sustainable development of energy is an important guarantee for the sustainable development of economy and society today, and it is also a hot topic that scientific research pays close attention to[1]. The research of new generation energy conversion devices and energy storage equipment has become an urgent task, and the development of new energy sources such as fuel cells[2] and metal air cells[3] depends on the catalyst of oxygen reduction reaction. Traditional Pt-based catalysts have high catalytic activity in electrocatalytic oxygen reduction[4], but the high cost of Pt metal, limited resources, poor long-term stability and other factors constrain the large-scale commercial application[5].
Non-metallic catalysts can not only reduce the cost of catalysts, but also maintain high electrocatalytic oxygen reduction activity[6]. In the actual fuel cell test, nitrogen-doped carbon materials showed better catalytic activity and stability than Pt-based catalysts[7]. On this basis, doping metal single atom (M-NC) on the surface of nitrogen-containing carbon materials can further improve the catalytic activity of the materials. The active site on the surface of this kind of catalyst is MN2 site[8-10]. Among them, Fe-NC shows excellent catalytic performance in electrocatalytic oxygen reduction[11]. Precise regulation
of the structure of catalytic active sites can further optimize its catalytic performance. Doping impurity atoms, especially S atoms, on the surface of Fe-NC catalyst can regulate the electronic structure and improve its catalytic performance\textsuperscript{[12]}. S atom is similar to N atom, both of which are P-region elements, but their electronegativity and atomic radius show great difference. S atom has a relatively large atomic radius, so it is easy to introduce defects on the surface of carbon materials; in addition, the electronegativity of S atom is low, which can adjust the electronic structure of FeN\textsubscript{4} active site. Experimentally, S atoms can be introduced into N-doped carbon materials by pyrolysis of substances containing S molecules and salts at high temperature, such as Fe(SCN)\textsubscript{3}\textsuperscript{[13]}, CS(NH\textsubscript{2})\textsubscript{2}\textsuperscript{[14]}, zinc-dithiocarbamate\textsuperscript{[15]} and melamine-benzyl disulfide resin\textsuperscript{[16]}; or plasma treatment and chemical vapor deposition\textsuperscript{[17]}.

There are three main factors to improve the catalytic performance of electrocatalytic oxygen reduction reaction: (1) improve the overall conductivity of the catalyst; (2) improve the ability of active sites to adsorb oxygen; (3) reduce the electrocatalytic overpotential to improve the activity of the catalyst. S atom doping Fe-NC can significantly improve the catalytic performance of its electrocatalytic oxygen reduction reaction. However, the specific regulation mechanism of S atom doping on the catalytic performance of Fe-NC is still unclear. Therefore, it is necessary to deeply and systematically study the mechanism of S atom doping on catalytic performance. In this work, the structure and stability of S atom doped Fe-NC, the electronic structure of the catalyst, the adsorption of oxygen at the active site and the mechanism of oxygen reduction at the active site were studied by using density functional theory.

![Figure 1](image_url)

**Figure 1.** The optimized structures of FeN\textsubscript{4} and FeNS\textsubscript{x}.

Note: Blue spheres represent nitrogen atoms, yellow spheres represent sulfur atoms, and gray spheres represent iron atoms, shown here. The number is the length of the Fe-n1 bond.

### 2. Results and discussion

#### 2.1 Structure and stability of FeNS

A large number of studies have shown that the catalytic active center of monatomic iron-doped nitrogenous carbon materials is FeN\textsubscript{4} site, that is, iron monatoms coordinate with four pyridine nitrogen, as shown in Figure 1\textsuperscript{[18–21]}. Therefore, the Fe-NC catalyst we studied adopts the same FeN\textsubscript{4} model as that in the literature, and studies the possible configuration of S atom doping on this basis. According to the research of Li et al.\textsuperscript{[12]}, when the ratio of S atom to N atom is \(n(S) : n(N) = 1:1\), the catalytic activity of FeNS catalyst for oxygen reduction reaction is the highest. In order to study the influence of S doping ratio, we consider the config-
uration of 1 ~ 4 S atom doping. As shown in Figure 1, there are two possible configurations of an S atom doping, namely, S atom is bonded to N atom (FeNS1a) and S atom is not bonded to N atom (FeNS1b). The value of formation energy is less than zero, indicating that the structure is thermodynamically stable, and the value of formation energy is greater than zero, indicating that the structure is unstable. According to the formation energy calculation (Table 1), the formation energy of FeNS1a is $-0.06$ eV, and the formation energy of FeNS1b is $0.50$ eV. The stability of structure FeNS1a is better than that of structure FeNS1b. Therefore, FeNS doped with 2–4 S atoms only considers the direct bonding structure between S atoms and N atoms. In FeNS2 structure, the formation energy of introducing two S atoms is $-0.27$ eV, which shows that its thermodynamic stability is better than FeNS1a structure. Further increasing the amount of S atoms doping can further improve the stability of the catalyst structure. When introducing four S atoms doping at FeN4 site, the formation energy of the structure is $-1.74$ eV. The calculation results of formation energy show that introducing S atom doping around FeN4 site can improve the stability of catalyst structure. By calculating the Fe-N bond length, it is found that sulfur atom doping has a great influence on the Fe-N bond length. The bond length of Fe-N bond in FeN4 structure is 0.188 nm, while the bond length of Fe-N in FeNS1a and FeNS1b is 0.183 nm and 0.189 nm, respectively, and the bond length of Fe-N in FeNS2 structure is 0.183 nm, the Fe-N bond length in FeNS1a and FeNS2 configurations is significantly shortened, at which time all atoms are still in the same plane. In the FeNS3 structure, the Fe-N bond length is 0.187 nm, and in the FeNS4 structure, the Fe-N bond length is 0.201 nm. In this case, because the atomic radius of the S atom is larger than that of the nitrogen atom, the doping of too many S atoms leads to the emergence of vacancies. At this time, one of the S atoms breaks the bond with the N atom.

### Table 1. Formation energy of catalysts and specific calculation parameters

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E(\text{FeNSx})$/eV</th>
<th>$\mu(\text{C})$/eV</th>
<th>$\mu(\text{S})$/eV</th>
<th>$E(\text{FeN4})$/eV</th>
<th>$E_f$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNS1a</td>
<td>$-421.13$</td>
<td>$-9.26$</td>
<td>$-0.94$</td>
<td>$-429.40$</td>
<td>$-0.06$</td>
</tr>
<tr>
<td>FeNS1b</td>
<td>$-420.58$</td>
<td>$-9.26$</td>
<td>$-0.94$</td>
<td>$-429.40$</td>
<td>$0.50$</td>
</tr>
<tr>
<td>FeNS2</td>
<td>$-413.02$</td>
<td>$-9.26$</td>
<td>$-0.94$</td>
<td>$-429.40$</td>
<td>$-0.27$</td>
</tr>
<tr>
<td>FeNS3</td>
<td>$-404.91$</td>
<td>$-9.26$</td>
<td>$-0.94$</td>
<td>$-429.40$</td>
<td>$-0.49$</td>
</tr>
<tr>
<td>FeNS4</td>
<td>$-397.82$</td>
<td>$-9.26$</td>
<td>$-0.94$</td>
<td>$-429.40$</td>
<td>$-1.74$</td>
</tr>
</tbody>
</table>

### Table 2. Bader charge analyses of catalysts

| Element | FeN4 (|e|) | FeNS1a (|e|) | FeNS2 (|e|) | FeNS3 (|e|) | FeNS4 (|e|) |
|---------|-------|----------|----------|----------|----------|
| Fe      | $-1.08$ | $-1.05$  | $-1.02$  | $-0.90$  | $-1.14$  |
| N       | 1.11   | 1.17     | 1.17     | 1.18     | 1.21     |
| S1      | $-0.75$ | $-0.77$  | $-0.78$  | $-0.78$  | $-0.72$  |
| S2      | $-0.81$ | $-0.70$  | $-0.95$  | $-0.83$  | $-0.42$  |
| S3      | $-0.81$ | $-0.70$  | $-0.95$  | $-0.83$  | $-0.42$  |

2.2 Study on the electronic structure of Fe-NS catalyst

In order to study the effect of S atom doping on the electronic structure of FeN4 catalyst, we calculated the Bader charges of five studied structures. Bader charge analysis is shown in Table 2. The electron transfer number of iron atom in FeN4 structure is 1.08 |e| after introducing an S atom, the electron transfer number of Fe atom becomes 1.05 |e|. After introducing two S atoms, the number of electrons transferred by Fe atoms to the surrounding is 1.02 |e| in FeNS3 structure, the number of electrons transferred by Fe atoms to the surrounding is 0.90 |e|. But in FeNS4 structure, the number of electrons lost by Fe atoms is 1.14 |e| which is higher than the number of electrons transferred in other structures. Therefore, in FeNS4 structure, the valence state of Fe is higher than that of Fe in FeN4. Next, we further analyze the bonding between Fe atoms and the surrounding coordination environ-
ment by using the density of electronic states, as shown in Figure 2. Because the outermost electron plays a major role in the actual bonding process, only 3d orbital is considered for Fe atom, and only 2p orbital is considered for N atom and S atom. The results show that the electron density of the 3d orbit of Fe atom on the surface of FeN₄ catalyst is large, and the obvious electron spin phenomenon occurs in the 3d orbit of Fe atom. Due to the strong orbital interaction, the spin up orbit shifts about 2.0 eV below the Fermi level, resulting in only the spin down orbit near the Fermi level, and the band gap of this spin down orbit at the Fermi level is 0.907 eV. After introducing an S atom doping, the band gap of the catalyst is significantly reduced, and in FeNS₁a, the band gap is 0.449 eV. The introduction of 2p orbital of S atom does not cause 3d orbital hybridization of Fe atom, but it will reduce the band gap of catalyst energy band. When more S atoms are introduced, the band structure shows the same rule. The band gap of FeNS₂ catalyst is 0.351 eV, FeNS₃ catalyst is 0.254 eV, and FeNS₄ catalyst is 0.121 eV. The density of electronic states and energy band analysis show that the higher the proportion of S atoms doped in FeN₄ catalyst, the narrower the band gap of the electronic structure of the catalyst, so as to enhance the conductivity of the catalyst, which is more conducive to the transfer of electrons in the process of electrocatalysis. Therefore, the introduction of S atoms into FeN₄ catalyst can significantly improve the electron transfer rate of the catalyst.

Figure 2. Densities of states of (a) FeN₄, (b) FeNS₁a, (c) FeNS₁b, (d) FeNS₂ and (e) FeNS₃.
2.3 Oxygen adsorption mechanism

The adsorption capacity of the catalyst for oxygen is very important to the overall oxygen reduction performance of the catalyst. The adsorption configuration and adsorption energy of oxygen on different catalyst surfaces are shown in Figure 3. We found two oxygen adsorption configurations, named side-on and end-on adsorption configurations, respectively. In the side-on adsorption configuration, two oxygen atoms in the O₂ molecule are bonded to the substrate. In the end-on adsorption configuration, the oxygen molecule is vertically adsorbed on the catalyst surface, and one of the oxygen atoms is connected to the catalyst. On the surface of FeN₄, oxygen tends to be adsorbed on the catalyst surface in the end-on configuration, with an adsorption energy of −2.03 eV, and its side-on adsorption configuration has an adsorption energy of −1.93 eV. Compared with the adsorption on the surface of FeN₄ catalyst, the adsorption of oxygen on the surface of FeNS₁ catalyst is more stable, indicating that the introduction of an S atom doping on the surface of FeN₄ catalyst can improve the adsorption capacity of oxygen, thereby improving the activation performance of oxygen molecules. The calculation results show that in a catalyst doped with S atom, oxygen tends to be adsorbed on the catalyst surface in a side-on adsorption configuration. On FeNS₁a catalyst, its adsorption energy is −2.18 eV, and the proportion of S atom doping continues to increase. Compared with a catalyst doped with S atom, the adsorption energy of oxygen gas decreases. On the surface of FeNS₂ catalyst, oxygen tends to be in side-on adsorption configuration, with an adsorption energy of −2.16 eV, and oxygen in end-on configuration has an adsorption energy of −2.06 eV. On the surface of FeNS₃ catalyst, oxygen has only end-on adsorption configuration, and its adsorption energy is −1.97 eV, which is lower than that of oxygen on the surface of FeN₄ catalyst. On the surface of FeNS₄ catalyst, the adsorption configuration of oxygen is end-on, and the adsorption energy is −1.97 eV. The study of oxygen adsorption on the surface of S-atom doped Fe-NC catalyst shows that the introduction of a small amount of S-atom doping can improve the ability of the catalyst to adsorb oxygen, and increase the proportion of S-atom doping will reduce its ability to adsorb oxygen.

<table>
<thead>
<tr>
<th></th>
<th>End-on adsorption</th>
<th>Side-on adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeN₄</td>
<td><img src="image" alt="FeN₄ side-on adsorption" /></td>
<td><img src="image" alt="FeN₄ end-on adsorption" /></td>
</tr>
<tr>
<td>FeNS₁</td>
<td><img src="image" alt="FeNS₁ end-on adsorption" /></td>
<td><img src="image" alt="FeNS₁ side-on adsorption" /></td>
</tr>
<tr>
<td>FeNS₂</td>
<td><img src="image" alt="FeNS₂ end-on adsorption" /></td>
<td><img src="image" alt="FeNS₂ side-on adsorption" /></td>
</tr>
<tr>
<td>FeNS₃</td>
<td><img src="image" alt="FeNS₃ end-on adsorption" /></td>
<td><img src="image" alt="FeNS₃ side-on adsorption" /></td>
</tr>
<tr>
<td>FeNS₄</td>
<td><img src="image" alt="FeNS₄ end-on adsorption" /></td>
<td><img src="image" alt="FeNS₄ side-on adsorption" /></td>
</tr>
</tbody>
</table>

Figure 3. The optimized adsorption configurations of oxygen.
2.4 Study on the mechanism of oxygen reduction reaction

We studied the catalytic activity of oxygen reduction at the active site of the catalyst. According to Li et al.\[12\], the reduction reaction of oxygen on the surface of Fe-NS catalyst generates water through four electronic reaction steps. Therefore, we mainly study this mechanism. In the calculation of reaction free energy, because VASP is not accurate enough to calculate the vibration frequency of diatomic gas molecules, we use the method applied by Nørskov et al.\[22\] to subtract the free energy of the other three reaction steps from the standard electrode potential of oxygen reduction reaction to obtain the reaction free energy of the first step: \( \text{O}_2 + \ast + (\text{H}^+ + e^{-}) \rightarrow \ast \text{OOH} \). The equilibrium electrode potential of the oxygen reduction reaction is 4.92 V. In order to significantly represent the overpotential of the oxygen reduction reaction, we calculated the reaction free energy when \( U = 1.23 \text{ V} \). The reaction intermediates involved in the oxygen reduction reaction are \( \ast \text{OOH} \), \( \ast \text{O} \) and \( \ast \text{OH} \) (\( \ast \) indicates that the intermediates are adsorbed on the catalyst surface). The free energy diagram of oxygen reduction reaction is shown in Figure 4, the adsorption configuration of reaction intermediates involved in the reaction process is shown in Figure 5, and the specific free energy of reaction is shown in Table 3. On the surface of FeN4 catalyst, oxygen is stably adsorbed on the top of the iron atom in the end-on configuration. A proton electron pair in the solution is transferred to the oxygen molecule, and the proton is connected with the distal oxygen atom to form an OOH\(^*\) intermediate. The free energy of this step is \(-0.27 \text{ eV}\), which is spontaneous. Next, the OOH\(^*\) intermediate receives a pair of protons electrons to generate a water molecule and an adsorbed oxygen atom O\(^*\). The reaction free energy of this step is \(-0.91 \text{ eV}\), which is also spontaneous, indicating that once oxygen is adsorbed on the FeN4 surface, it will automatically form O\(^*\) and a water molecule. Next, O\(^*\) generates OH\(^*\) through proton electron reaction, which needs to overcome the energy of 0.48 eV. Finally, a proton is transferred to the O atom to generate a water molecule, which needs to overcome the energy of 0.70 eV. The last step is the potential control step of oxygen reduction reaction, which shows that the overpotential of oxygen reduction reaction on FeN4 catalyst is 0.70 V. In FeNS1a and the active site, the potential control step of oxygen reduction reaction is also the last step, and the over potential is 0.79 V, indicating that the introduction of an S atom does not reduce the over potential of oxygen reduction reaction, but increases the over potential. On the surface of FeNS2 catalyst, due to the weak adsorption capacity of OOH\(^*\), the initial reaction requires large energy, which is 0.21 eV. The potential control step of oxygen reduction reaction is OH\(^*\) + (H\(^+\) + e\(^-\)) \(\rightarrow \ast + \text{H}_2\text{O}(l)\), and the overpotential is 0.82 V. On the surface of FeNS3 catalyst, the potential control step is the same as that on FeN4 surface, and the over potential is 0.77 V. On the surface of FeNS4 catalyst, the potential control step is also the last step, and the over potential is 0.68 V. Among the five studied catalysts, the over potential is the lowest. Compared with Barder charge analysis, the valence state of Fe is the highest in FeNS4 catalyst, indicating that the higher oxidation state of Fe can reduce the adsorption of reaction intermediate OOH\(^*\).

Table 3. Reaction energies of oxygen reduction reaction

<table>
<thead>
<tr>
<th></th>
<th>( \Delta G_1/\text{eV} )</th>
<th>( \Delta G_2/\text{eV} )</th>
<th>( \Delta G_3/\text{eV} )</th>
<th>( \Delta G_4/\text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeN4</td>
<td>-0.27</td>
<td>-0.91</td>
<td>0.48</td>
<td>0.70</td>
</tr>
<tr>
<td>FeNS1a</td>
<td>0.06</td>
<td>-1.38</td>
<td>0.52</td>
<td>0.79</td>
</tr>
<tr>
<td>FeNS2</td>
<td>0.21</td>
<td>-1.61</td>
<td>0.57</td>
<td>0.82</td>
</tr>
<tr>
<td>FeNS3</td>
<td>0.01</td>
<td>-1.09</td>
<td>0.32</td>
<td>0.76</td>
</tr>
<tr>
<td>FeNS4</td>
<td>-0.17</td>
<td>-0.80</td>
<td>0.29</td>
<td>0.68</td>
</tr>
</tbody>
</table>

3. Conclusion

Based on density functional theory, the electronic regulation mechanism of introducing sulfur atom doping on the surface of FeN4 catalyst was calculated and studied. The results are as follows.

1) Doping S atoms on the surface of FeN4 catalyst can improve the stability of the catalyst. The higher the proportion of doped S atoms, the more stable the catalyst is.
(2) S atom doping can reduce the band gap of FeN₄ catalyst, improve the conductivity, facilitate the transfer of electrons in the process of oxygen reduction reaction, and facilitate the electrocatalytic reaction. When an S atom is introduced around the FeN₄ active site, the band gap is reduced from 0.907 eV to 0.449 eV, and the conductivity is significantly improved.

(3) Compared with FeN₄ structure, the adsorption capacity of oxygen in the two structures of FeNS₁ is significantly improved. On this basis, increasing the proportion of S atom doping will reduce its oxygen adsorption capacity. Therefore, introducing a small amount of S atom doping into FeN₄ can improve the adsorption capacity of catalyst for oxygen.

(4) The study on the mechanism of oxygen reduction reaction shows that the introduction of four S atoms on the surface of FeN₄ catalyst to form FeNS₄ site can reduce the oxygen reduction overpotential and improve the activity of the catalytic site.

4. Calculation method

All calculations were performed using spin polarized density functional theory (DFT) and Vi-
enna ab initio simulation package (VASP)\textsuperscript{[23]}. This study uses the Perdew-Burke-Ernzerhof (PBE) exchange correlation function under the generalized gradient approximation (GGA)\textsuperscript{[24]}. In order to describe ionic nuclei, projection plus plane wave (PAW) pseudopotential is applied\textsuperscript{[23]}. The \textit{k}-point of geometric optimization is set to $5 \times 5 \times 1$. The \textit{k}-point calculated by DOS is set to $20 \times 20 \times 1$. The cutoff energy is 500 eV. The convergence criteria of electron energy and force are $10^{-5}$ eV and 0.01 eV/Å, respectively. Van der Waals interaction is considered when Grimme (DFT-D3) method is used. In our calculation, VASP implicit solvent model is used to consider the influence of water\textsuperscript{[25]} to simulate the real electrocatalytic environment.

The thermodynamic stability of the catalyst is calculated by the formation energy ($E_f$):

$$E_f = E(\text{FeNSe}) + m\mu(C) - n\mu(S) - E(\text{FeN}_{12})$$

Where $E$ (total) represents the energy of the catalyst after S atom doping, and $E$ (graphite) represents the energy of the complete carbon material, $\mu(C)$, $\mu(S)$, $\mu(Fe)$ represents the chemical potential of C atom, S atom and Fe atom, respectively. The chemical potential of carbon atom is obtained by removing the number of C atoms from the energy of complete carbon material, \(m\) represents the number of carbon atoms that need to be removed from the surface of carbon material to obtain the target catalyst, and \(n\) represents the number of sulfur atoms in the catalyst. The stability of catalyst structure can be obtained through the above formula. If the formation energy of catalyst is less than zero, it indicates the thermodynamic stability of catalyst.

The adsorption energy ($E_{\text{ads}}$) of oxygen and reaction intermediates is calculated as follows:

$$E_{\text{ads}} = E_{\text{M/S}} - E_S - E_M$$

$E_{\text{M/S}}$, $E_S$ and $E_M$ respectively represent the total energy of the system after adsorption, the energy of the catalyst before adsorption and the energy of the adsorbate\textsuperscript{[26]}.

The calculated hydrogen electrode (CHE) model is used to calculate the change of Gibbs free energy ($\Delta G$). In the CHE model, the following reactions are in equilibrium with the reversible hydrogen electrode at 0 V at all pH values.

$$\text{H}^+ (\text{aq.}) + e^- \rightleftharpoons \frac{1}{2}\text{H}_2 (g)$$

Therefore, when calculating its free energy, the basic step $^*A + H^+ + e^- \rightarrow ^*AH$ can be replaced by $^*A + 1/2\text{H}_2 (g) \rightarrow ^*AH$. The free energy ($G$) of each state is shown in formula (4):

$$G = E + ZPE + \int C_p dT - TS + G_{\text{pH}}$$

Where $T$ is the temperature and $E$ is the electron energy. $ZPE$, $\int C_p dT$ and $TS$ respectively contribute zero energy to molecular vibration, enthalpy change from 0 to 7K and entropy correction at 298.15 K. they are obtained on the basis of vibration frequency analysis. $G_{\text{pH}}$ is the free energy correction of pH, which can be calculated by $G_{\text{pH}} = k_B T \ln10*\text{pH}$, and the pH value is assumed to be 0\textsuperscript{[27]} in this work. $G(U) = G(0 \text{ V}) - neU$ is used to calculate the free energy related to the applied potential ($U$).

In this work, the reaction free energy when $U = 1.23 \text{ V}$ is calculated, and the over potential is defined as the maximum reaction free energy change, namely:

$$\eta = \frac{\Delta G_{\text{max}}(G_1, G_2, G_3, G_4)}{n e}$$

Where $n$ is the number of electrons transferred during the reaction.

**Acknowledgements**

The project was supported by the Major Scientific and Technological Projects of China National Petroleum Corporation (ZD2019-184-001) and Fundamental Research Funds for the Central Universities (18CX02042A and 18CX05011A).

**Conflict of interest**

The authors declared no conflict of interest.

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