CHAPTER 9

First Principles Modelling of New Catalyst for Oxygen Reduction Reaction
9.1. Introduction:

As already discussed earlier, slow kinetics of the oxygen reduction reaction (ORR) at the cathode is found to be one of the limiting factors for better performance of the fuel cells and the conventional platinum based catalysts make the fuel cell very expensive. Hence, there is a need to find an alternate non-platinum based catalyst for large scale commercialization of fuel cells.\textsuperscript{98-100}

There are a large number of non-precious metal based catalysts viz. transition metals (Fe, Co, etc.), metal oxides, metal carbides, as well as metal free catalysts like carbon materials, boron and nitrogen doped carbon nanomaterials, graphitic carbon nitride, etc.\textsuperscript{283-286} One of the metal free catalysts which is extensively studied is the graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}). However, the catalytic activity of simple g-C\textsubscript{3}N\textsubscript{4} is found to be poor, which is attributed to the poor electrical conductivity of g-C\textsubscript{3}N\textsubscript{4}.\textsuperscript{287} To improve the activity, different kinds of carbon materials have been mixed with g-C\textsubscript{3}N\textsubscript{4} and it has been shown that as compared to pristine g-C\textsubscript{3}N\textsubscript{4}, the carbon composites are more active towards ORR.\textsuperscript{287-289} Zheng et al.\textsuperscript{289} have shown that g-C\textsubscript{3}N\textsubscript{4}@carbon can catalyze the ORR reaction with better activity which is explained by considering the enhanced electron transfer efficiency. Transition metal (TM) complexes of macrocyclic systems like phthalocyanines and porphyrines, especially the N\textsubscript{4}-TM complexes of cobalt (Co) and iron (Fe) are another class of materials extensively studied for ORR catalysis.\textsuperscript{289-292} It has been shown that the transition metal complexes of porphyrine-like carbon nanotubes and graphitic materials can exhibit excellent activity towards ORR.\textsuperscript{293-294}

In the present study, we have carried out a detailed investigation on the ORR catalytic activity of transition metal decorated graphyne. In a recent study, Kong et al.\textsuperscript{295} have shown that, on boron doping, graphyne can be made active for ORR whereas the pristine graphyne is inactive. He et al.\textsuperscript{296} studied the adsorption of different 3d-transition metals on graphyne and
showed that TM doping not only modulates the electronic structure, but can also incorporate excellent magnetic properties. Earlier studies have shown that the ferromagnetic nature present in the platinum group metal electro catalysts improves the ORR catalytic activity.\textsuperscript{297} Inspired from these earlier studies, we have doped graphyne with three different TMs, viz. Fe, Co and Ni to study the adsorption of possible ORR intermediates on these metal decorated graphyne systems.

We have also explored another important material, silicene\textsuperscript{298-300}, the silicon counterpart of the well known graphene as a metal free catalyst for ORR. The possible existence of silicene with puckered atomic arrangement in honeycomb fashion had been proposed some time back and its synthesis has also been reported recently.\textsuperscript{301-304} After the synthesis of silicene on a substrate like Ag (111) surface, the number of studies on this interesting material has increased drastically and it is shown to have applications in different fields of science and technology.\textsuperscript{305-306} The presence of small puckering in the silicene indicates that it can be more reactive as compared to the graphene and therefore we are interested in studying the ORR catalytic activity of free standing silicene single layer as well as the double layers. Recently, Padova et al.\textsuperscript{307} investigated the room temperature oxidation of silicene nanoribbons through photo emission spectroscopy and they have shown that the oxidation starts at very high oxygen exposures indicating the stability of silicene towards oxidation. Later, Molle et al.\textsuperscript{308} have also shown that silicene is stable upon exposure up to 1000 L of ultrapure O\textsubscript{2}, but it undergoes progressive oxidation in air and they have demonstrated different ways of encapsulating it to hinder the oxidation. In view of this, we are also interested to study the ORR mechanism on both single and bilayers and find the differences.
9.2. Computational details

All the electronic structure calculations have been carried out through the spin-polarized periodic DFT as implemented in the VASP.\textsuperscript{131-132} PAW\textsuperscript{129-130} based potentials were used with a plane-wave basis cutoff energy of 550 eV. GGA of PBE\textsuperscript{103} has been used to treat the exchange-correlation energy density functional, $E_{xc} [\rho]$. Throughout the calculations, an energy cutoff of $1 \times 10^{-6}$ eV is set as the convergence criteria for the electronic self-consistent field iterations. Geometry optimizations have been carried out at constant volume until the Hellmann–Feynman force component on each atom is less than 0.01 eV Å\textsuperscript{-1}. The Brillouin zone has been sampled using the automatically generated Gamma centered 9 × 9 × 1 Monkhorst-Pack set of k points.\textsuperscript{133} The atomic charges have been calculated through the Bader\textsuperscript{192} charge density analysis. The initial geometries and all reported structures have been obtained using the graphic software MOLDEN.\textsuperscript{135}

9.3. Results and Discussion.

9.3.1 Transition Metal Decorated Graphyne: An Efficient Catalyst for Oxygen Reduction Reaction

Before studying the adsorption of TMs on graphyne, we have optimized the graphyne structure with a unit cell of 12 carbon atoms. To study the adsorption of TMs on this structure, we have considered different possible sites, like above the C\textsubscript{6} ring, above the C-C bond, above the C atom and above the cavity. Most preferred site for metal binding is found to be above the cavity as shown in Figure 9.1 where the metal can bind with six sp carbon atoms. We have considered three TMs viz. Fe, Co and Ni for adsorption and the optimized geometries are given in Figure 1 with the corresponding results reported in Table 9.1. In TM decorated graphyne systems, the cell parameters are found to increase as compared to pristine graphyne as reported in Table 1 and the variation is maximum in Fe-graphyne system. The adsorption energy per metal atom of Fe is calculated to be -4.52 eV whereas it is -5.26 eV in Co and Ni decorated
systems. In all the systems, the metal binding energies are found to be higher than the cohesive energies of the corresponding metals. The calculated magnetic moments show that the Fe and Co decorated systems are magnetic in nature whereas the Ni-graphyne system is diamagnetic in nature, which is in consistency with the earlier report. In the case of Fe-graphyne system, the metal atom is found to be slightly above (~0.15 Å) the carbon plane and in cases of Co and Ni decorated systems, the metal atoms are almost in the plane of carbon atoms.

Table 9.1: Graphyne-TM binding energy, O₂ adsorption energy, metal-carbon distance, metal-oxygen distance and O-O bond length as calculated through the PBE method.

<table>
<thead>
<tr>
<th>System</th>
<th>Cell parameter (Å)</th>
<th>ΔEₘ (eV)</th>
<th>ΔE₀₂ (eV)</th>
<th>Lₘ₋C (Å)</th>
<th>Lₘ₋O (Å)</th>
<th>L₀₋₀ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂-Fe</td>
<td>6.981</td>
<td>-4.52</td>
<td>-0.91</td>
<td>1.963</td>
<td>1.744</td>
<td>1.286</td>
</tr>
<tr>
<td>C₁₂-Co</td>
<td>6.963</td>
<td>-5.26</td>
<td>-0.58</td>
<td>1.947</td>
<td>1.858</td>
<td>1.278</td>
</tr>
<tr>
<td>C₁₂-Ni</td>
<td>6.950</td>
<td>-5.26</td>
<td>-0.01</td>
<td>1.956</td>
<td>2.824</td>
<td>1.242</td>
</tr>
</tbody>
</table>

Figure 9.1. Optimized geometries of 3 x 3 x 1 super cell structures of (a) GY-Fe (b) GY-Co and (c) GY-Ni

3.2 Adsorption of molecular oxygen on graphyne-TM complex

One of the rate limiting steps of ORR observed in most of the catalysts is the adsorption of O₂ molecule on the catalyst surface. Here, we have studied the adsorption of O₂ on all three metal decorated graphyne systems. We have considered different possible sites for O₂ adsorption and found that adsorption above the metal site is the most preferred site as shown in Figure 9.2. In the case of Fe decorated system, the O₂ adsorption energy is found to be -0.91 eV and the O-O bond distance is found to be stretched to 1.286 Å from the value 1.233 Å in
free O₂. The corresponding binding energies in Co and Ni decorated systems are found to be -0.58 eV and -0.01 eV with the O-O distance of 1.278 and 1.242 Å respectively. The calculated atomic charges through Bader charge density analysis show that there is a charge transfer from the GY-TM system to the adsorbed oxygen which is relatively high (0.4) in Fe systems as compared to the Co system (0.35). This charge density analysis shows that electron transfer is taking place from metal d orbital to the anti-bonding oxygen orbitals. From the calculated magnetic moments on oxygen it is found that in the case of O₂ adsorbed on Ni-graphyne, the O₂ is having the same magnetic moment as that of the free molecule whereas for Co and Fe decorated systems, there is a drop in magnetic moment on oxygen. The observed order of reactivity Fe>Co>Ni is the same as that of their magnetic moments or available unpaired d-electron present in the system. These results show that graphyne-Ni system is not suitable for ORR catalyst and Fe-graphyne is better as compared to Co-graphyne system.

3.3 Oxygen reduction path on TM-graphyne in acid medium

A systematic study of the possible ORR paths is carried out on both Fe and Co decorated graphyne system. The Ni-graphyne system is omitted as the oxygen adsorption energy is very less in this case. As discussed in the previous section the O-O elongation in Fe
system is high as compared to the Co system and the stretching is comparable to that observed in TM-N_x (X= 2 or 4) chelates observed earlier. This reaction can be written as

\[ \text{GY-TM} + \text{O}_2 + 4 (\text{H}^+ + \text{e}^-) \rightarrow \text{GY-TM-OO} + 4 (\text{H}^+ + \text{e}^-) \]

and the calculated free energy changes (\(\Delta G_1\)) are found to be -0.92 eV and -0.65 eV for Fe and Co decorated systems respectively.

In the next reaction step, the adsorbed oxygen accepts hydrogen and forms OOH adsorbed on the metal site as shown below.

\[ \text{GY-TM-OO} + 4 (\text{H}^+ + \text{e}^-) \rightarrow \text{GY-TM-OOH} + 3 (\text{H}^+ + \text{e}^-) \]

The associated free energy change (\(\Delta G_2\)) is found to be -0.53 eV and -0.25 eV for Fe and Co decorated systems respectively. In these optimized structures, the O-O bond lengths are found to be 1.449 Å and 1.425 Å in Fe and Co decorated systems respectively. The observed TM-O

\[ \text{Figure 9.3. Optimized unit cell structures of (a) GY-Co-OOH (b) GY-Co-O-OH}_2 \text{ (c) GY-Co-OH-OH}_2 \text{ and (d) GY-Co-OH}_2-\text{OH}_2 \]

distances in Fe and Co decorated systems are found to be 1.812 Å and 1.859 Å respectively. Once the OOH species is formed, the adsorption of next hydrogen is possible on two oxygen sites. From the energies of the optimized structures, we have found that in both Fe and Co systems, the most favourable oxygen site is the one which is already bound to hydrogen and not the oxygen bonded to metal. This shows that in both the systems considered here, the ORR process proceeds through a more efficient four electron process and not through a two electron process where hydrogen peroxide intermediate is formed. This step can be represented as
GY-TM-OOH + 3(H⁺ + e⁻ ) → GY-TM-O + H₂O + 2(H⁺ + e⁻ ).

The free energy change (ΔG₃) for this reaction is calculated to be -2.24 eV and -1.95 eV on Fe and Co decorated systems respectively. The optimized geometry for this step on Co decorated system is given in Figure 9.3. After adsorption of two hydrogen atoms on oxygen site the O-O bond distances are found to be 2.829 Å and 2.836 Å on Fe and Co decorated systems respectively. This bond lengths show that in both the cases, the O-O bond is completely cleaved and one water molecule is generated. The TM-O bond distances are found to be 1.636 Å (Fe-O) and 1.671 Å (Co-O).

The adsorbed oxygen atom is found to react with another hydrogen to form OH adsorbed on the TM site as

GY-TM-O + 2(H⁺ + e⁻ ) → GY-TM-OH + (H⁺ + e⁻ )

and the free energy change (ΔG₄) for this step is found to be -0.78 eV and -0.99 eV on Fe and Co decorated systems respectively. The TM-O bond lengths are found to increase from the same in the previous intermediate and are found to be 1.814 Å (Fe-O) and 1.846 Å (Co-O). In the final step, the adsorbed OH species picks up one hydrogen and forms H₂O adsorbed as shown in Figure 9.3 which has to get desorbed ultimately and this can be shown as

GY-TM-OH + (H⁺ + e⁻ ) → GY-TM + H₂O

For this reaction, the free energy changes (ΔG₅) are calculated to be -0.44 eV and -1.08 eV on Fe and Co systems respectively. The TM-O distance in H₂O adsorbed on GY-TM system are found to be 2.239 Å (Fe-O) and 2.334 Å (Co-O) which are considerably higher than that observed in the previous intermediate. The free energies of all the five intermediate steps discussed above are given in Table 9.2 for both Fe and Co systems.
3.4 Oxygen reduction path on TM-graphyne in alkaline medium

In alkaline medium, the proposed ORR mechanism can be given as

\[
\text{GY-TM} + \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow \text{GY-TM-OOO} + 2\text{H}_2\text{O} + 4e^- \\
\text{GY-TM-OOO} + 2\text{H}_2\text{O} + 4e^- \rightarrow \text{GY-TM-OOH} + \text{OH}^- + \text{H}_2\text{O} + 3e^- \\
\text{GY-TM-OOH} + \text{OH}^- + \text{H}_2\text{O} + 3e^- \rightarrow \text{GY-TM-OOH}^- + \text{OH}^- + \text{H}_2\text{O} + 2e^- \\
\text{GY-TM-OOH}^- + \text{OH}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{GY-TM} + 4(\text{OH}^-)
\]

and the corresponding free energy changes for these four reaction steps can be assigned as \(\Delta G_1\) to \(\Delta G_4\).

The intermediate OOH\(^-\), the peroxide ion adsorbed on both Fe and Co decorated systems are shown in Fig-6. From the optimized geometry, it is found that in the case of GY-Fe, the O-O bond distance in the adsorbed OOH\(^-\) ion is elongated to 1.946 Å from 1.449 Å in OOH adsorbed. This O-O bond distance shows that the peroxide formation is not

Table 9.2: Calculated free energy changes (in eV) for different intermediate steps of ORR on GY-Fe and GY-Co in both acid and alkaline medium.

<table>
<thead>
<tr>
<th></th>
<th>In acid medium</th>
<th>In alkaline medium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GY-Fe</td>
<td>GY-Co</td>
</tr>
<tr>
<td>(\Delta G_1) (eV)</td>
<td>-0.92</td>
<td>-0.65</td>
</tr>
<tr>
<td>(\Delta G_2) (eV)</td>
<td>-0.53</td>
<td>-0.25</td>
</tr>
<tr>
<td>(\Delta G_3) (eV)</td>
<td>-2.24</td>
<td>-1.95</td>
</tr>
<tr>
<td>(\Delta G_4) (eV)</td>
<td>-0.78</td>
<td>-0.99</td>
</tr>
<tr>
<td>(\Delta G_5) (eV)</td>
<td>-0.44</td>
<td>-1.08</td>
</tr>
</tbody>
</table>

Figure 9.4 Optimized unit cell structures of (a) GY-Fe-OOH\(^-\) and (b) GY-Co-OOH\(^-\)
energetically favourable and the O-O bond is almost dissociated indicating that the ORR is proceeding through a more efficient four electron reduction. In the case of the GY-Co system, the corresponding O-O bond distance in the adsorbed OOH\(^-\) ion is calculated to be 1.459 Å which is very close to the O-O bond distance in hydrogen peroxide. This result shows that the ORR on GY-Co proceeds through two electron mechanism by the formation of hydrogen peroxide. Free energies for all the four proposed intermediate steps for both the systems are reported in Table 9.2. From the results discussed above, one can understand that the GY-Fe system is more efficient catalyst for ORR as compared to GY-Co in both acid and alkaline mediums.

9.3.2 Silicene: a metal-free catalyst for ORR

In this study, we have mainly studied the electronic structure of single and bilayer silicene and their electro catalytic activity towards the ORR. We have optimized the basic hexagonal unit cell of silicene containing two silicon atoms whose 3x3x1 supercell is shown in Figure 9.7(a). The optimized cell parameter is found to be 3.868 Å and the Si-Si bond length is calculated to be 2.278 Å. The optimized structure of silicene is found to have a puckered structure with a puckering constant (distortion along z-direction) of 0.45 Å and the puckering angle is found to be 37.81°. The calculated electronic band

![Figure 9.5](image-url) Optimized geometries of the 3x3x1 super cell in (a) top view and (b) side view along with the band dispersion plot of the silicene
structure as obtained through the PBE method is shown in Fig 9.7(c), which shows a zero band gap along the \textit{k-point} 'K' similar to graphene. The buckling nature present in silicene has been earlier explained by Jose et al. through pseudo-Jahn-Teller effect due to the strong coupling between the unoccupied and occupied molecular orbitals and also it is attributed to the weak interaction between the \(\pi\) orbitals because of the large Si-Si distance. To model the bilayer silicene, we have considered two different modes of stacking, viz. AA and AB modes. The optimized structures of both the conformations are shown in Figure 9.8. From the energy values calculated through PBE method, the AA mode is found to be energetically more favourable as compared to the AB mode. Interestingly, the AA double layer contains two perfectly planar silicene sheets stacked one above the other with an inter-planar distance is of 2.412 Å showing a strong bonding, which is in accordance with the earlier report. The in plane Si-Si bond length of double layer is found to get increased to 2.386 Å from 2.278 Å in a single layer. In the case of AB conformer, the puckering angle is found to increase to 53.06\(^\circ\) from 37.81\(^\circ\) in single layer with the inter- and intra-planar Si-Si bond distances of 2.524 Å and 2.322 Å respectively. As the system changes from non-planar buckled structure to a perfectly planar, as one goes from single layer to double layer, the two cases are expected to show different reactivity.

**Figure 9.6:** Optimized super cell structures of silicene double layer in AA and AB stacking mode.
**O₂ adsorption**

We have considered different possible sites for O₂ adsorption on silicene viz. above a Si atom and perpendicular to the plane, above the center of the Si₆ ring, above the Si-Si bond and perpendicular to plane, above the Si-Si bond and parallel to the plane. Among all these sites, O₂ adsorption on Si-Si bond and parallel to the plane is found to be energetically more favourable. The optimized minimum energy structure of O₂ adsorbed on silicene for single layer and bilayer, are shown in Figure 9.9. The O-O distance in O₂ adsorbed on single and bilayer silicene are found to be 1.513 Å and 1.511 Å respectively which is considerably elongated from 1.233 Å in free O₂. The Si-O bond distance in single and bilayer cases are found to be 1.727 Å and 1.742 Å respectively. The corresponding binding energy of oxygen on silicene single and double layers, as calculated through the PBE method is found to be -1.82 eV and -2.68 eV respectively. As shown in Figure 9.9, upon adsorption of O₂ on single layer silicene, one of the Si atoms is found to move down and in the case of double layer, two of the Si atoms to which the oxygen atoms are bonded are lifted up and the two corresponding Si atoms in the lower layer are pressed down.

![Figure 9.7: Optimized cell structures of O₂ adsorbed on single layer and bilayer silicene](image)

199
Now, we discuss the different possible intermediate steps of ORR in acid medium. A systematic study of the ORR process on both single and bilayer silicene has been carried out and the corresponding geometries are reported in Figures 9.10 and 9.11 respectively. The first step in ORR is the $\text{O}_2$ adsorption as already discussed in earlier and it can be written as

$$\text{Si} + \text{O}_2 + 4 (\text{H}^+ + \text{e}^-) \rightarrow \text{^{*}OO} + 4 (\text{H}^+ + \text{e}^-)$$

where, the $^*$ indicates adsorbed (on silicene) and the calculated free energy change of this reaction on single and bilayer is found to be -1.92 eV and -2.71 eV respectively. Once the $\text{O}_2$ is adsorbed, it picks up a proton and electron to form $\text{OOH}$ adsorbed on the surface. The optimized geometries of the $\text{OOH}$ adsorbed on single and bilayer show that the O-O bond is completely broken. On the single layer, one of the oxygen atom is found to move to bridging position on one of the Si-Si bonds with the OH adsorbed on one Si atom site and the measured O-O bond distance is found to be 4.773 Å. However, on the bilayer, the oxygen does not move to the bridging position but stays on one Si atom with OH adsorbed on another Si atom as shown in Figure 9.11. The measured O-O distance is found to be 2.717 Å and the hydrogen of OH is found to form hydrogen bonding with the adsorbed oxygen atom with a H--O distance of 1.807 Å. In both the cases, it is observed that the O-O bond is completely broken indicating that there is no way for the formation of $\text{H}_2\text{O}_2$ intermediate observed in the two electron path and the ORR will follow a more efficient four electron reduction path. This reaction can be represented as

$$\text{^{*}OO} + 4(\text{H}^+ + \text{e}^-) \rightarrow \text{^{*}O} - \text{^{*}OH} + 3(\text{H}^+ + \text{e}^-)$$

**Figure 9.8:** Possible intermediates in ORR on silicene single layer
and the corresponding free energy of this reaction on single and bilayer are calculated to be -3.53 and -3.00 eV respectively.

As a next step of the reaction we have considered two possible sites for the next hydrogen attack, i.e on the *O and *OH sites. In both the cases, hydrogen is found to prefer to bind on *O site as shown in Figures 9.10 and Figure 9.11. In case of single layer, as it is shown in Fig 9.10, one of the *OH is bridge bonded to Si-Si bond with Si-O bond distance of 1.904 Å whereas the other *OH is bonded to one Si atom with Si-O bond distance of 1.679 Å. In the case of bilayer, both the *OH are bonded to adjacent Si atoms and the shortest Si-O bond distance is found to be 1.679 Å. This reaction can be given as

\[
*O - *OH + 3(H^+ + e^-) \rightarrow *OH - *OH + 2(H^+ + e^-)
\]

and the change in free energy of this reaction on single and bilayer silicene are calculated to be +0.43 eV and -0.87 eV respectively. In the next reaction step, one of the *OH get converted to water by capturing a proton and electron which can be represented as

\[
*OH - *OH + 2(H^+ + e^-) \rightarrow *OH_2 - *OH + (H^+ + e^-)
\]

**Figure 9.9:** Possible intermediates in ORR on bilayer silicene

In the case of single layer silicene, it is seen that the *OH on Si-Si bridge is the preferred site for hydrogen and the water molecule formed moves away from the surface, forming hydrogen bonding with the other *OH group as shown in Figure 9.10. In the case of bilayer also, the water molecule formed is found to move away from the silicene surface, forming a hydrogen
bond with the adsorbed OH group. The free energy change for this reaction step on single and double layer are found to be -0.14 and +0.75 eV respectively. In the final step of the reaction, the remaining *OH reacts with a proton and electron to form the second water molecule which can be written as

\[ *\text{OH}_2 - *\text{OH} + (\text{H}^+ + \text{e}^-) \rightarrow \text{Si} + 2\text{H}_2\text{O} \]

The free energy change for this step on single and double layers is calculated to be +0.24 and +0.91 eV respectively. This positive free energy changes indicate that the desorption of the water molecule from the surface is energetically uphill.

### 9.4 Conclusions

In summary, we have shown here that the binding energies of all the three transition metals to graphyne are higher than the corresponding metal cohesive energies. Fe and Co decorated systems are found to adsorb molecular oxygen whereas Ni decorated system is inactive. In acid medium, the ORR on both GY-Fe and GY-Co systems is found to proceed through the more efficient four electron reduction mechanism. In alkaline medium, ORR on GY-Fe system is shown to follow a four electron reduction path whereas on GY-Co system ORR proceeds by two electron reduction path through the formation of hydrogen peroxide. In the case of silicene system, we have shown that the ORR on both single layer and double layer will be through the four electron path.