The oxygen reduction reaction (ORR) plays an important role in fuel cell devices and holds a major place in the field of electrocatalysis. The reaction mechanism has, so far, been explored with the Pt electrode, which, however, due to its high cost and limited resources, limits the practical application of Pt in fuel cell. As an alternative to Pt electrode, metallophthalocyanine is currently under research focus as suitable electrocatalysts, because of the presence of delocalized and conjugated π bond in metal-phthalocyanine, making it suitable for oxidation and reduction reaction. Among various phthalocyanines, Iron Phthalocyanine (FePc) shows best catalytic activity toward reduction of oxygen. Therefore, in this report, we have studied for the first time the electronic structure of FePc nanoribbon as well as its electrochemical activity in alkaline solution. The ORR activity for FePc nanoribbon is comparable to the state-of-the-art Pt/C catalyst. First principle DFT calculation suggests the hybridization between dπ orbital of Fe 3d with 2p orbital of O in adsorbed O2 molecule. Our results demonstrate that FePc nanoribbon may be used as a promising electrocatalyst in fuel cells as an alternative to Pt-based catalyst.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium.16 Mukherjee et al. have synthesized ZnPc nanostructure and RGO/Zn Penanocomposite and studied their electrochemical property in 0.1 M KOH solution. The ORR study revealed that the composite material showed superior catalytic activity, which is attributed to the synergistic effect between ZnPc and RGO.17

As CoPc and FePc are known to have good electrocatalytic activities due to their redox active central metal atom, there are many reports available based on them. However, in most of the commercially available reports, metal phthalocyanine material have been used to study ORR activity. To the best of our knowledge, there is no report so far on the electrochemical properties of FePc nanostructures. Herein, we have carried out the ORR mechanism on FePc nanoribbon in alkaline medium in the presence and absence of an external potential using first principle DFT calculation. A model of the ORR proposed previously has been used as the starting point for the exploration of the ORR behavior of FePc nanostructure.18 Additionally, DFT calculation demonstrates the mechanism that governs the catalytic activity, which in turn suggests the hybridization between Fe 3d orbital and O 2p orbital.

### Computational Methods

We have used the Vienna Ab initio Simulation Package (VASP) to calculate total energy values of optimized structures.19,20 The plane wave basis with projector augmented wave (PAW) potential was used.21 Generalized gradient approximation (GGA) of Perdew- Burke- Ernzerhof (PBE) is used for the exchange-correlation potential and a plane-wave kinetic energy cutoff of 500 eV is used here.22 Van der Waals correction has been incorporated in calculating the total energies of intermediates using Grimme’s DFT-D2 dispersion correction, as supported by VASP.

In this study, the extending direction of FePc nanoribbon was chosen along z-direction. The distance between two nearest ribbons along y-direction was set to 25 Å. Also, a vacuum of 10 Åwas incorporated along z-direction. For geometry optimization, 5 × 1 × 1 k-mesh has been used via Monkhorst-Pack scheme. 11 × 1 × 1 k-points has been taken for density of state (DOS) calculation.
The adsorption energies of different intermediates on the catalyst surface in the course of ORR pathway has been calculated in each step. The adsorption energy (\(E_{\text{ad}}\)) is defined as follows:

\[
E_{\text{ad}} = E_{\text{FePcNR−ads}} - (E_{\text{FePcNR}} + E_{\text{ads}})
\]

If \(E_{\text{ad}}\) is negative, the adsorption on the catalyst surface would be energetically favorable. The ORR electrocatalytic activity is governed by the adsorption of intermediates including \(\text{O}_2\), \(\text{OH}\), \(\text{O}\), \(\text{OH}\). At the liquid–solid interface, the realistic details of the microscopic phenomena are strongly challenging in the ab initio scheme.\(^{23}\) Taking the reference potential to be that of standard hydrogen electrode (SHE), one can relate the chemical potential of the reaction (\("\text{H}^+ + e^-\)”) to that of \(1/2 \text{H}_2\) in equilibrium i.e. it has been assumed that “\(\text{H}^+ \text{H}^+\)” is in equilibrium with \(1/2 \text{H}_2\) at pH 0 and 0 V potential in SHE.\(^{24-26}\) The one electron reduction process is considered to be a coupled proton and electron transfer (CPET). The applied potential (U) is taken through a displacement of Fermi level of the electrocatalyst used at cathode. This approach permits us to shift in free energy values by \(-eU\) for each intermediate steps (27). In this work, we have carried out the calculations in alkaline medium, i.e. at pH = 14, as described in earlier literature.\(^{28}\) The equilibrium potential (U(0)) is 0.40 V with respect to the SHE.

In earlier reports of ORR, most of the theoretical studies have been performed by considering the reaction in gas-phase environment which matched well with hydrogen oxidation reactions. However, in practical fuel cell applications, the solvation effect cannot be ignored. Recent studies have showed that solvation effect can play a crucial role in controlling the reaction barriers significantly.\(^{29,30}\) Thus, to make the calculation precise, a solvent environment is required which can be modeled either by adding explicit water molecules or an entire water bilayer.\(^{29}\) But in this paper, we limit our study within gas-phase environment (without solvation) because of instrumental limitation.

**Results and Discussion**

The optimized structure of FePc nanoribbon extended along x-direction is represented in Figure 1. One unit cell of the nanoribbon contains twenty-six C atoms, ten H atoms, eight N atoms, and one Fe atom. The lattice parameters for the unit cell of FePc nanoribbon are found to be \(a = 10.65 \, \text{Å}, b = 25.13 \, \text{Å}, c = 9.90 \, \text{Å}\). Each Fe atom makes bond with four N atoms with bond length \(\sim 1.93 \, \text{Å}\) which agrees well with the experimental data.\(^{32}\)

The oxygen reduction reaction starts with the adsorption of \(\text{O}_2\) molecule onto the FePc nanoribbon catalyst surface. To begin with, the \(\text{O}_2\) molecule was taken to be adsorbed onto FePc nanoribbon via two different configurations, namely, side-on and end-on configurations. The most stable end-on configuration for \(\text{O}_2\) molecule is presented in Figure 2. Here, one O atom is bonded with central Fe atom with bond length \(\sim 1.77 \, \text{Å}\) and adsorption energy \(\sim 1.02 \, \text{eV}\). The bond length increased from initial 1.23 Å to 1.28 Å. In order to investigate the clear insight of this step, electronic structure calculation has been carried out which resulting in the split-off of bonding and antibonding state of d\(^z^2\) orbital of Fe atom in FePc nanoribbon catalyst surface. Figure 3a showed the spin polarized partial density of states (PDOS) for the 3d electrons of Fe in FePc catalyst before and after \(\text{O}_2\) adsorption which clearly indicates that this orbital has a major contribution in ORR activity of FePc nanoribbon. Bader charge analysis also showed that about \(\sim 0.29 \, \text{e}^-\) charge has been transferred from central Fe atom to O atom. Figure 3b depicted the strong hybridization between d\(^z^2\) orbital of Fe atom with 2p orbital of O atom in spin-up and spin-down direction.

We have further examined the ORR steps on the FePc nanoribbon surface. After the chemisorption of \(\text{O}_2\) molecule, adsorption of a proton coupled with an electron formed an \(\text{OOH}\) group adsorbed on the Fe site (Figure 3a). This step initiated the scission of \(\text{O}–\text{O}\) bond as the bond length was increased from 1.28 Å to 1.46 Å. Further hydrogenation by adsorbing another proton coupled with an electron leaded to the formation of \(\text{OH}^-\), leaving behind one \(\text{O}\) atom bonded with central Fe atom with bond length \(\sim 1.64 \, \text{Å}\). The corresponding adsorption energy became \(\sim 5.19 \, \text{eV}\). Finally, \(\text{OH}\) group has been formed after reacting with other proton coupled with an electron with adsorption energy \(\sim 2.89 \, \text{eV}\). The overall 4\(^{\text{e}^-}\) pathway in the alkaline medium is as follows:

\[
\begin{align*}
\text{FePc} + \text{O}_2 + 2\text{H}_2\text{O}(l) + 4\text{e}^- & \rightarrow \text{FePc} - \text{O}_2 + 2\text{H}_2\text{O}(l) + 4\text{e}^- \quad [1] \\
\text{FePc} - \text{O}_2 + 2\text{H}_2\text{O}(l) + 4\text{e}^- & \rightarrow \text{FePc} - \text{OOH} + (\text{OH})^- \\
& + \text{H}_2\text{O}(l) + 3\text{e}^- \quad [2] \\
\text{FePc} - \text{OOH} + (\text{OH})^- + \text{H}_2\text{O}(l) + 3\text{e}^- & \rightarrow \text{FePc} - \text{O} \\
& + 2(\text{OH})^- + \text{H}_2\text{O}(l) + 2\text{e}^- \quad [3] \\
\text{FePc} - \text{O} + 2(\text{OH})^- & \rightarrow \text{FePc} - \text{OH} \\
& + 3(\text{OH})^- + \text{e}^- \quad [4] \\
\text{FePc} - \text{OH} + 3(\text{OH})^- + \text{e}^- & \rightarrow 4(\text{OH})^- + \text{FePc} \quad [5]
\end{align*}
\]

Here, (l) denotes the liquid state and (●) denotes the adsorbed species on FePc surface. The atomic configuration of reaction pathway as well as the reaction intermediates are shown in Figure 4. The adsorption...
energies in each step of the reaction have been calculated accordingly and are presented in Table I.

To explore the free energy profile along the ORR pathway, the change in Gibbs free energy for all intermediates has been evaluated using the following relation:

$$
\Delta G = \Delta E - T \Delta S - neU
$$

where $\Delta E$, the change in reaction energy, can be considered as total energy calculated from DFT. $\Delta S$, the change in entropy, can be obtained directly from a physical chemistry table. $n$ represents the number of transferred electrons, and $U$ is the operating electrochemical potential in standard hydrogen electrode (SHE). In order to calculate the change in entropy ($\Delta S$) of the molecules, $O_2$, $H_2$ and $H_2O$ molecules are considered to be in gas phase at room temperature and under ambient pressure. It is also considered that the entropy of the adsorbed states of the molecules are negligible compared to that in their gas phase. Although, earlier reports claimed that entropies of the adsorbed states of the molecules can make difference in the reaction energy diagram, there are also some reports, where, these entropies were neglected in the energy calculations. The free energies of $H_2O$, $O_2$ (g) and $OH^-$ are estimated from the following equations:

$$
G_{H_2O(l)} = G_{H_2O(g)} + RT \ln \left( \frac{P}{P_0} \right) \quad [7]
$$

$$
G_{O_2(g)} = 2G_{H_2O(l)} - 2G_{H_2} + 4.92 \text{ eV} \quad [8]
$$

$$
G_{OH^-} = G_{H_2O(l)} - G_{H^+} = G_{H_2O(l)} - \left( \frac{1}{2} \right) G_{H_2} + K_b T \ln (10) \times pH \quad [9]
$$

Figure 3. (a) PDOS of dz^2 orbital of Fe atom before and after O_2 adsorption (b) hybridization of Fe-dz2 orbital with O-2p orbital.

Figure 4. Optimized structure of different intermediates along the ORR reaction pathway.

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**Table I. Summary of the different parameters in the ORR steps.**

| Intermediates | $E_{\text{ads}}$ (eV) | $d_{O-O}$ (Å) | $d_{Fe-O}$ (Å) |
|---------------|-------------------|---------------|---------------|
| $O_2$         | −1.02             | 1.28127       | 1.77590       |
| OOH           | −1.94             | 1.46182       | 1.76150       |
| $O^-$         | −5.19             |               | 1.64241       |
| OH$^-$        | −2.89             |               | 1.78960       |

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Where $R$ is the gas constant, $T = 298.15$ K, $p = 0.035$ bar and $p_0 = 1$ bar.

As indicated earlier, in this free energy analysis, “$\text{H}^+ + \text{e}^-\text{" has been assumed to be in equilibrium with } 1/2 \text{H}_2,$ at $\text{pH} 0$ and $0$ V potential in SHE. Let us now examine the ORR reaction pathway on FePc nanoribbon as shown in Figure 5. At Zero cell potential, when the first electron is transferred leading to the formation of $\text{OOH}^*$ attached on the catalyst surface, the change in free energy is slightly exothermic ($\sim 0.07$ eV), i.e, downhill as shown in Figure 5a. In the next step, when the second electron is transferred which initiate the O-O bond cleavage and formation of $\text{O}^*$ attached on the catalyst surface, the free energy change is highly exothermic by $\sim 1.50$ eV. Being exothermic, it affirmed that the second electron transfer step does not lead to the formation of $\text{H}_2\text{O}_2$. The third electron transfer that forms $\text{OH}^*$ attached on the catalyst, the change in free energy is endothermic ($\sim 0.008$ eV) i.e, uphill in the free energy profile. Again, the last step is exothermic and subsequently resulting in the formation of $\text{OH}^-$. Therefore, the adsorption of the third electron requires a small energy barrier of $0.008$ eV. At equilibrium potential ($U = 0.4$ V vs. SHE) as shown in Figure 5c, the first electron transfer is endothermic and the required reaction energy is $\sim 0.33$ V. The second electron transfer step is highly exothermic followed by the other two endothermic electron transfer steps with required reaction energies $\sim 0.408$ eV and $\sim 0.364$ eV respectively. Hence, the maximal value (operating potential) at which all the steps are exothermic, i.e, expected to occur spontaneously (downhill in the free energy profile), is estimated to be $0.008$ V ($0.82$ V) versus SHE (RHE). Therefore, the third step is the potential determining step with overpotential $\sim 0.408$ V ($0.41$ V) versus SHE (RHE), i.e, this step is the rate limiting step that requires an activation barrier of $\sim 0.408$ eV. To benchmark the ORR activity of FePc nanoribbon, we compare our results with the Pt (111) surface. The experimentally reported value of operating potential for Pt (111) is $< 0.9$ V.$^{27}$ Using the same computational parameters, we have estimated the value of operating potential and overpotential of Pt (111) surface and are found to be $0.8$ V and $0.4$ V respectively which are same as mentioned in the earlier report.$^{18}$ The free energy diagram of Pt (111) surface is shown in Figure 6. All these results indicated that the values of these parameters for FePc is comparable with that of Pt(111) surface and hence FePc nanoribbon can be a viable alternative to the conventional Pt based electrocatalyst.

Figure 5. Free energy diagram of FePc nanoribbon at an applied potential (versus SHE) (a) $U = 0$ V (b) $U = -0.83$ V (c) $U = 0.4$ V and (d) $U = -0.008$ V.

Figure 6. Free energy diagram of Pt(111) in alkaline medium.
Conclusions

We have successfully demonstrated the electrocatalytic behavior toward ORR of the FePc nanoribbon surface using first principle DFT calculation. Here, the adsorption energies of different reaction intermediates and thermodynamics for oxygen reduction reaction on phthalocyanine nanoribbon are explored systematically. The results suggest that the Fe-3dz² orbital played the major role in ORR activity showing splitting in bonding and antibonding state. In addition to that, the hybridization between Fe-3dz² orbital with O-2p orbital indicated the charge transfer between central Fe atom in phthalocyanine and O atom in O₂ molecule. The FePc nanoribbon in this study follows 4-electron reduction pathway. The overpotential calculated for this system has been estimated as 0.41 V (RHE). In all, the above results obtained from theoretical calculations indicate that FePc nanoribbon is a highly efficient electrocatalyst for ORR with the best price-performance, making it one of the most promising alternatives to traditional Pt-based electrocatalysts for large-scale industrial applications in fuel cells.

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