Structure of Iron Oxides FeO\textsubscript{n} with High Oxygen Content

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Objectives

The aim of this study is to understand capabilities of iron atoms for binding multiple oxygen species (O, O$_2$, and O$_3$). Subtasks include:

♦ How many oxygen units can bind to a Fe atom;
♦ Structure and geometrical stability of monoiron oxides;
♦ What is the electron affinity of FeO$_n$? Are the FeO$_n^-$ anions candidates for fabricating new materials with high oxygen content?
♦ What is the thermodynamic stability of neutral and singly negatively charged monoiron oxides?
Background of Problem

- High-capacity batteries were fabricated using $\text{K}_2\text{FeO}_4$ and $\text{BaFeO}_4$ as cathodes and Zn as anode (Science 285, 1039 (1999)).

- Salts containing $\text{FeO}_4$ and sodium ferrate $\text{Na}_4\text{FeO}_5$ are good oxidizers and are used for environmental purification purposes.

- $\text{FeO}_6$ octahedra were observed in a number of inorganic salts. In particular, clusters $\text{Fe(H}_2\text{O})_6$ are building blocks in the $\text{K}_2[\text{Fe(H}_2\text{O})_6](\text{SO}_4)_2$ salt.
Energetic Super-Iron Battery

In Fe-based batteries, metallic Zn is an anode and KOH is an electrolyte as in conventional (not rechargeable) alkaline batteries that have MnO₂ as a cathode. The half-reactions in alkaline batteries are:

\[
\text{Zn (s) + 2OH}^{-} (\text{aq}) \rightarrow \text{ZnO (s) + H}_2\text{O (l) + 2e}^{-} \\
2\text{MnO}_2 \text{ (s) + H}_2\text{O (l) + 2e}^{-} \rightarrow \text{Mn}_2\text{O}_3 \text{ (s) + 2OH}^{-} (\text{aq})
\]

\(s=\text{solid, } I=\text{intermediate, } aq = \text{aquatic}\)

The super-iron are rechargeable batteries provide > 50% more energy capacity. The super-iron battery discharge proceeds as:

\[
\text{FeO}_4^{2-} + 3\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{FeOOH} + 5\text{OH}^{-} \quad \text{or} \quad \\
\text{FeO}_4^{2-} + 5/2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow 1/2\text{Fe}_2\text{O}_3 + 5\text{OH}^{-}
\]

At higher oxygen content, more charge carriers OH⁻ can be produced.
Technical Approach

- Gaussian 03 program was used. For the atomic orbitals, we have used the standard contracted 6-311+G(3df) basis: \textbf{10s7p4d3f1g} for Fe and \textbf{5s4p3d1f} for O atoms.

- The primary exchange-correlation functional is comprised of the Becke's exchange and Perdew-Wang's correlation (BPW91).

- A number of DFT and hybrid HF/DFT functionals were tested.

- Each optimization was followed by computations of harmonic vibrational frequencies in order to confirm that the optimization arrived at a stationary point on the potential energy surface.
Computation quality

In order to test reliability of the BPW91/ 6-311+G(3df) approach we compared the results of our computations with experimental data.

Spectroscopic constants of O$_2$:

BPW91: $r_e = 1.218$ Å $\omega_e = 1557$ cm$^{-1}$

Experiment: $r_e = 1.207$ Å $\omega_e = 1563$ cm$^{-1}$

Electron affinity:

<table>
<thead>
<tr>
<th></th>
<th>BPW91</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>0.405 eV</td>
<td>0.448 ± 0.006 eV</td>
</tr>
<tr>
<td>FeO$_3$</td>
<td>3.25 eV</td>
<td>3.31 ± 0.06 eV</td>
</tr>
<tr>
<td>FeO$_4$</td>
<td>3.69 eV</td>
<td>3.84 ± 0.04 eV</td>
</tr>
</tbody>
</table>
Structures of FeO$_5$ and FeO$_5^-$

There are a large number of states that are close in total energy.

Iron atom carries a magnetic moment.

An example of spin-induced dissociation in the FeO$_5^-$ anion.
Competition of oxo, peroxo, superoxo and ozonide groups in neutral FeO$_6$ and FeO$_7$

Generally, the presence of ozonide groups leads to higher total energy. Increase in oxygen content leads to larger number of isomers and higher density of states.
The lowest total energy configurations of FeO$_8^-$ and FeO$_{10}^-$

The largest number of closely spaced states are found for $n = 8$ and $9$. At larger $n$, the number of possible isomers sharply decreases. No O rings beyond three-atom ozonides are found.
The lowest total energy configurations of FeO$_{11}^-$ and FeO$_{12}^-$

A few geometrically stable configurations are found for $n=11$ and $n=12$. The preferred configuration for FeO$_{12}^-$ is composed of 6 peroxo group. Geometrically stable states for FeO$_{12}^-$ and its anion do exist up to spin multiplicities $M=2S+1 = 12$. 

![Diagram of FeO$_{11}^-$ and FeO$_{12}^-$ configurations](image)
Adiabatic electron affinities of FeO\textsubscript{n} computed at the BPW91 level of theory using two basis sets.

<table>
<thead>
<tr>
<th></th>
<th>6-311+G\textsuperscript{*}</th>
<th>6-311+G(3df)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO\textsubscript{3}</td>
<td>3.33</td>
<td>3.25\textsuperscript{a}</td>
</tr>
<tr>
<td>FeO\textsubscript{4}</td>
<td>3.79</td>
<td>3.69\textsuperscript{b}</td>
</tr>
<tr>
<td>FeO\textsubscript{5}</td>
<td>4.15</td>
<td>3.95</td>
</tr>
<tr>
<td>FeO\textsubscript{6}</td>
<td>3.78</td>
<td>3.56</td>
</tr>
<tr>
<td>FeO\textsubscript{7}</td>
<td>3.59</td>
<td>3.57</td>
</tr>
<tr>
<td>FeO\textsubscript{8}</td>
<td>3.54</td>
<td>3.24</td>
</tr>
<tr>
<td>FeO\textsubscript{9}</td>
<td>3.85</td>
<td>3.50</td>
</tr>
<tr>
<td>FeO\textsubscript{10}</td>
<td>3.52</td>
<td>3.48</td>
</tr>
<tr>
<td>FeO\textsubscript{11}</td>
<td>3.84</td>
<td>3.80</td>
</tr>
<tr>
<td>FeO\textsubscript{12}</td>
<td>3.76</td>
<td>3.69</td>
</tr>
</tbody>
</table>

All values are in eV.
\textsuperscript{a} Experimental value is 3.31±0.06 eV (adiabatic).
\textsuperscript{b} Experimental value is 3.84±0.04 eV (vertical).

Some FeO\textsubscript{n} behaves as halogens and some as weak superhalogens. All of them are capable to serve as counterions in salts.
Dissociation Energies of FeO\textsubscript{n} Through Different Decay Channels (in eV)

<table>
<thead>
<tr>
<th>Channel</th>
<th>(D_0)</th>
<th>Channel</th>
<th>(D_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{FeO}_4\rightarrow \text{FeO}_2 + \text{O}_2)</td>
<td>1.88</td>
<td>(\text{FeO}_9\rightarrow \text{FeO}_7 + \text{O}_2)</td>
<td>0.15</td>
</tr>
<tr>
<td>(\rightarrow \text{FeO}_3 + \text{O})</td>
<td>3.21</td>
<td>(\rightarrow \text{FeO}_6 + \text{O}_3)</td>
<td>1.17</td>
</tr>
<tr>
<td>(\text{FeO}_5\rightarrow \text{FeO}_3 + \text{O}_2)</td>
<td>0.03</td>
<td>(\text{FeO}_{10}\rightarrow \text{FeO}_8 + \text{O}_2)</td>
<td>(-0.01)</td>
</tr>
<tr>
<td>(\rightarrow \text{FeO}_2 + \text{O}_3)</td>
<td>3.11</td>
<td>(\rightarrow \text{FeO}_4 + 3\text{O}_2)</td>
<td>(-0.93)</td>
</tr>
<tr>
<td>(\text{FeO}_6\rightarrow \text{FeO}_4 + \text{O}_2)</td>
<td>(-0.50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\rightarrow \text{FeO}_5 + \text{O})</td>
<td>2.68</td>
<td>(\text{FeO}_{11}\rightarrow \text{FeO}_9 + \text{O}_2)</td>
<td>(-0.69)</td>
</tr>
<tr>
<td>(\text{FeO}_7\rightarrow \text{FeO}_5 + \text{O}_2)</td>
<td>(-0.65)</td>
<td>(\rightarrow \text{FeO}_4 + 2\text{O}_2 + \text{O}_3)</td>
<td>0.04</td>
</tr>
<tr>
<td>(\rightarrow \text{FeO}_4 + \text{O}_3)</td>
<td>0.58</td>
<td>(\rightarrow \text{FeO}_8 + \text{O}_3)</td>
<td>0.96</td>
</tr>
<tr>
<td>(\text{FeO}_8\rightarrow \text{FeO}_6 + \text{O}_2)</td>
<td>(-0.42)</td>
<td>(\text{FeO}<em>{12}\rightarrow \text{FeO}</em>{10} + \text{O}_2)</td>
<td>(-0.56)</td>
</tr>
<tr>
<td>(\rightarrow \text{FeO}_4 + 2\text{O}_2)</td>
<td>(-0.92)</td>
<td>(\rightarrow \text{FeO}_4 + 4\text{O}_2)</td>
<td>(-1.48)</td>
</tr>
<tr>
<td>(\rightarrow \text{FeO}_7 + \text{O})</td>
<td>2.91</td>
<td>(\rightarrow \text{FeO}_{11} + \text{O})</td>
<td>2.89</td>
</tr>
</tbody>
</table>

All FeO\textsubscript{n} with \(n>4\) are metastable. There are a number of exothermic channels for each \(n>5\), the final decay products consist of FeO\textsubscript{4} and O\textsubscript{2} if \(n\) is even or O\textsubscript{2} and ozone O\textsubscript{3} if is odd.
Summary
G. L. Gutsev, C. A. Weatherford, K. Pradhan, P. Jena, J.

The results of our computations performed using density functional theory with generalized gradient approximation (DFT-GGA) for the neutral and negatively charged FeO$_n$ species show that there are geometrically stable isomers for each $n$ in the range from $n = 5$ to 12.

The isomer states do correspond to local minima and are unstable toward release of dioxygen for $n > 5$. All the neutral species do possess rather large electron affinities ranging from 3.24 eV to 3.95 eV and the anions can potentially serve as counterions in salts if a proper cation is found. Such salts would possess a high oxidative power.
First results on highly rich oxides of other 3d-metal atoms

\[ \begin{align*}
\text{TiO}_8 & \quad 2S+1=5 \\
\text{VO}_8 & \quad 2S+1=2 \\
\text{CrO}_8 & \quad 2S+1=3 \\
\text{MnO}_8 & \quad 2S+1=4 \\
\text{ScO}_8 & \quad 2S+1=4 \\
\text{FeO}_8 & \quad 2S+1=1 \\
\text{CuO}_8 & \quad 2S+1=2 \\
\text{ZnO}_8 & \quad 2S+1=3 \\
\text{CoO}_8 & \quad 2S+1=2 \\
\text{NiO}_8 & \quad 2S+1=1
\end{align*} \]

Competition between peroxo- and superoxo-O\(_2\) in the lowest energy states of MO\(_8\) (M=Sc-Zn)