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14. ABSTRACT

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Report Title

Interaction between Oxygen and Molten Carbonate: A DFT Study

ABSTRACT

Student Senior Thesis by Gladney Arianna
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Interaction between Oxygen and Molten Carbonate: A DFT Study

By

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Major: Chemistry

Advisor: Dr. Changyong Qin

Benedict College, Columbia, SC

November 2011

Abstract

The interaction between oxygen and selected molten carbonates has been examined in this project using density functional theory (DFT) modeling. In particular, B3LYP/6-31G(d) has been used for all geometry optimization, charge calculation, and orbital analysis. Three oxygen species including molecular oxygen (O_2), superoxide (O_2^-), peroxide (O_2^{2-}) and atomic oxygen ion (O^{2-}) are considered. The combination of oxygen with single carbonate (CO_3^{2-}) forms molecular complexes, CO_5^{2-} and CO_4^{2-}, respectively.

For CO_4^{2-}, the planar trigonal structure is 260.0 kJ/mol lower in energy than the tetrahedral one. The calculated enthalpy change of $2CO_3^{2-} + O_2 \rightarrow 2\ CO_4^{2-}$ is -19.4 kJ/mol, implying CO_4^{2-} as a likely intermediate. In CO_5^{2-}, the O-O distance is stretched to 1.321 Å , 0.106 Å longer than in the gas phase dioxygen. The total charge of O_2 is -0.672 e, indicating partial reduction of oxygen upon binding to carbonate. The binding energy of O_2 to CO_3^{2-} is 105.3 kJ/mol.

Structures of $(K_2CO_3)_4$, ($Li_2CO_3)_4$ and $(LiKCO_3)_4$ were also studied as simplest cluster models for molten carbonates with different compositions. Optimized average K-O and Li-O distances are 2.6602 Å and 1.9047 Å, which agrees well with the x-ray diffraction values of 2.7833 Å and 1.9947 Å, respectively. When one extra electron is attached to the clusters, DFT charge analysis shows that the electron density is shared by the alkali metals and these electrons will then be used to reduce the oxygen. In future, oxygen will be introduced to the carbonate clusters and its reduction will be studied in more detail. Therefore, we have found that the binding of oxygen to carbonate can promote the ORR in SOFCs and that $(K_2CO_3)_4$, $(Li_2CO_3)_4$ and $(LiKCO_3)_4$ will be the simplest cluster models to study the ORR process in SOFCs.

CONTENTS

1. Introduction

1.1 Fuel Cell

Fuel Cells are devices that convert chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent. All fuel cells consist of an anode, cathode and an electrolyte allowing positive and negative charges to flow from each side of the fuel cell. The anode is a negative electrode through which electric currents flow into an electrical device. The anode is typically the thickest and strongest layer in each cell because it is often the layer that provides mechanical support. The role of anode is to oxidize the fuel using the oxygen ions that diffuse through the electrolyte. For example, anode reaction for hydrogen as fuel feed,

$$H_2 + O^{2-} \longrightarrow H_2O + 2e^- \qquad \text{(Eq. 1)}$$

The electrolyte is a dense layer of ceramic that conducts oxygen ions. Its role is to transfert oxide from cathode to anode. The cathode is positive electrode through which electric currents flow from an electrical device back to the cell. Typical cathode reaction is

$$\tfrac{1}{2} O_2 + 2e^- \longrightarrow O^{2-} \quad . \qquad \text{(Eq. 2)}$$

It is a thin porous layer where oxygen reduction takes place. An electric circuit is externally displayed on the fuel cell which produces direct current electricity as part of the chemical reaction that takes place within a fuel cell. Fuel cells are classified by the material of electrolyte used and the fuel being oxidized. Solid Oxide Fuel Cells, as shown in Figure 1, are electrochemical devices that produce electricity directly from oxidizing a fuel such as hydrogen.

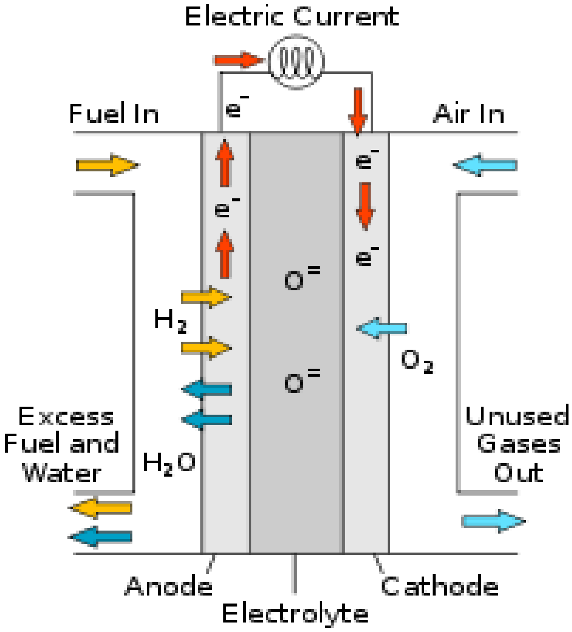


Figure 1: Solid Oxide Fuel Cell Process

Advantages of this class of fuel cell, as compared with other types of fuel cells, include high-efficiency, long term stability and fuel flexibility. Being that this type of fuel cell operates at extremely high temperatures, it can use pure H_2 and CO without being poisoned. The largest disadvantage is that such a high operating temperature results in a longer start-up time and chemical compatibility issues. Therefore solid oxide fuel cells cannot be used for smaller applications such as automobiles and handheld devices. Solid oxide fuel cells are of growing interest due to high efficiency in their one-step conversion of chemical energy to electricity. They function by having molecular oxygen come in and react with electrons at the cathode to form oxygen anions. These anions are then transported through the electrolyte to the anode to react with fuel which produces two electrons and byproduct water. An electric volt is generated by the potential difference between the electrons produced at the cathode and the cycle continues allowing fuel cell operation. The fuel cell itself has no moving parts, which makes it a quiet and reliable source of power. Strontium-doped lanthanum manganese (LSM) and yttria-stabilized zirconia (YSZ) have been adopted as the ion conducting material for the cathode and electrolyte of the particular solid oxide fuel cell being studied. LSM is the cathode material and YSZ is an excellent oxygen ion conductive electrolyte. A successful cathode material is determined by good electronic and ionic conductivity, high catalytic activity for ORR, low chemical interaction with the electrolyte and good chemical stability. LSM was adopted above other cathode materials because of its good chemical stability and high compatibility with YSZ. The problem with this fuel cell is that the oxygen reduction reaction is largely limited due to the small surface area of the triple phase boundary. The triple phase boundary is defined as a small line between the LSM/YSZ interface, the place at which the oxygen is actually reduced, as shown below is Figure 2. The transportation rate of the oxygen ion from the cathode to the electrolyte is decreased, causing the entire reaction to be slowed down. The material of the electrolyte is another factor in the disadvantage of this type of fuel cell. The YSZ is an expensive electrolyte material which causes the fuel to have to operate at high temperatures in order to be efficient.

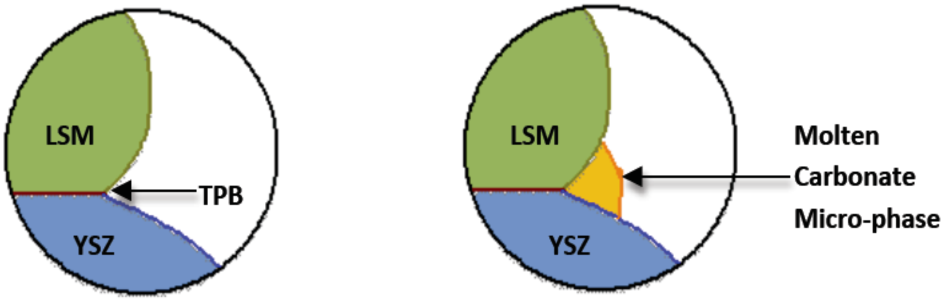


Figure 2: LSM/YSZ cathode

1.2 Carbonate

The promising efficiency and attractive environmental features of molten carbonate fuel cells have attracted major attention in recent years. Three oxygen/carbonate complexes, Li_2CO_3, $LiKCO_3$ and K_2CO_3, were chosen to determine how the molten carbonate phase will improve the ORR process and cell efficiency at low temperatures ranging from 500 °C to 650 °C. When heated to approximately 650 °C, these salts melt and become conductive to carbonate ions (CO_3^{2-}). These three complexes were chosen as a treatment to enhance the ORR because previous studies have shown that the melting point of molten lithium and potassium carbonate mixture at about 1:1 molar ratio is below 500 °C, which is ideal for the treatment of the LSM/YSZ cathode for low temperature SOFCs. Molten carbonate is of great importance to the LSM/YSZ cathode because the oxygen reduction and ion conduction mainly occur on the LSM surface. Cell performance is usually reduced by bad ionic conductivity on the LSM cathode, but if the molten carbonate phase can build an ionic bridge between LSM and YSZ, the problem could potentially be solved and cell performance will be largely improved. A major issue of the LSM/YSZ cathode is that at the Triple Phase Boundary (TPB), the transportation rate of the oxygen ion from the electrolyte to the cathode is largely limited due to small surface area. With the addition of molten carbonate to the cathode at the TPB, surface area would be increased which would increase rate of transportation and allow the fuel cell to operate at lower temperatures overall. The overall goal of this project is to understand the process of ORR on the LSM/YSZ cathode with the presence of molten carbonate and design next generation SOFCs with low operating temperature and cost.

1.3 DFT Method/Molecular Modeling

Density Functional Theory (DFT) method is defined as a quantum mechanical modeling method used in physics and chemistry to investigate the electronic structure (ground state) of many physical systems, in particular atoms and molecules. With this theory, the properties of systems can be determined using wavefunctions, which is the spatially dependent electron density. The name comes from the use of functions of the electrons. DFT is one of the most popular and versatile methods available in computational physics and computational chemistry. Since the 1970's, DFT has been very popular for calculations in solid state physics. However, DFT was not considered accurate enough for quantum chemistry until the 1990's, when the approximations used in the theory were greatly refined to better model for the exchange and correlation interactions. This hybrid tactic was devised by Axel Becke in 1993 in order to improve accuracy of this method. A variety of hybrid functionals (ex. B3LYP, PW91PW91 and B3PW91) take correlation from HF and other quantum mechanics methods used. In a number of cases, the results of DFT calculations agree quite well with experimental data. A bonus to the use of DFT is that computational costs are relatively low when compared to traditional methods, such as Hartree-Fock (HF). DFT calculations in gas phase will give beneficial and qualitative information about the chemical interactions at the TPB and improve our understanding of the oxygen reduction reaction mechanism. Previous studies have shown proof that DFT methods are accurate in assessing the electronic structure of different surface chemical systems such as vibrational frequency, electron transfer, charge distribution, reaction pathways and other properties that are difficult to assess experimentally. DFT methods have recently been improved and will provide molecular level information about the ORR process on the LSM/YSZ cathode. The reaction mechanism will be easily understood through DFT based *ab initio* calculations.

Molecular modeling is defined as the use of computational techniques and theoretical methods to provide a simplified view of the complex behavior of molecules. In computational chemistry, modeling gives scientists a visual insight into the process of molecules being studied and allows them to manipulate and gain insight into certain mechanisms. It describes the fundamental behavior of molecules mathematically. Molecular modeling can be applied to small systems as well as large molecules. To approach modeling, assumptions are formulated as to how a system operates that are then translated into equations. Quantum chemistry is a branch of theoretical chemistry that applies quantum mechanics. It determines the electronic behavior of atoms and molecules relating to their reactivity. Molecular modeling along with computational chemistry programs allow scientists to generate data including: geometries (bond distance, length & angles), energies (activation energy, heat of formation, bond energy) and electronic properties (charges, ionization, electron affinity). Molecular modeling makes it possible for the designing of new catalysts and technology advancements.

2. Computational Methods

2.1 Computational Method & Basis Set

Computational chemistry methods, mainly density functional theory (DFT), have proven to be accurate in assessing the electronic structure of different surface chemical systems, vibrational frequency, charge distribution, electron transfer, the path of reactions and other properties that are difficult to assess through experiment. The DFT based *ab initio* calculations for this work were calculated using B3LYP/6-31G(d) for oxygen and carbonate complexes while B3LYP/3-21G was used for the four unit carbonate complexes such as $(Li_2CO_3)_4$ and $(K_2CO_3)_4$. Basis set is a mathematical representation of the atomic orbitals within a molecule. This can be explained as restricting each electron to a certain region of space. The larger the basis set, the less constraint there is on electrons, therefore the molecular orbitals are more accurately represented. The 6-31G(d) basis set was chosen for oxygen & carbonate complexes. In this split valence basis, allowing more than one function per valence atomic orbital, the 1s core atomic orbitals are represented by six Gaussian type orbitals (GTO's), the valence 2s 2p atomic orbitals are represented by two basis functions, described by three GTO's and one GTO. The accuracy of bonding energies is improved by the addition of one set of polarizable functions, represented by the 'd'. The exact parameters in the 6-31G(d) basis set for Carbon and Oxygen are shown in Table 1 and 2 below.

```
BASIS "ao basis" PRINT
#BASIS SET: (11s,5p,1d) -> [4s,3p,1d]
C    S
  3047.5249000           0.0018347
   457.3695100           0.0140373
   103.9486900           0.0688426
    29.2101550           0.2321844
     9.2866630           0.4679413
     3.1639270           0.3623120
C    SP
     7.8682724          -0.1193324           0.0689991
     1.8812885          -0.1608542           0.3164240
     0.5442493           1.1434564           0.7443083
C    SP
     0.1687144           1.0000000           1.0000000
C    SP
     0.0438000           1.0000000           1.0000000
C    D
     0.8000000           1.0000000
```

Table 1. Carbon basis set 6-31G*

```
BASIS "ao basis" PRINT
#BASIS SET: (11s,5p,1d) -> [4s,3p,1d]
O    S
  5484.6717000           0.0018311
   825.2349500           0.0139501
   188.0469600           0.0684451
    52.9645000           0.2327143
    16.8975700           0.4701930
     5.7996353           0.3585209
O    SP
    15.5396160          -0.1107775           0.0708743
     3.5999336          -0.1480263           0.3397528
     1.0137618           1.1307670           0.7271586
O    SP
     0.2700058           1.0000000           1.0000000
O    SP
     0.0845000           1.0000000           1.0000000
O    D
     0.8000000           1.0000000
```

Table 2. Oxygen basis set 6-31G*

For the simple cluster model carbonate, $(Li_2CO_3)_4$ and $(K_2CO_3)_4$, the 3-21G basis set was used. The 1s core atomic orbitals are represented by 3 Gaussian type orbitals, the valence atomic orbitals are represented by two basis functions, 2 GTO's and 1 GTO respectively. The exact parameters in the 3-21^{++}G basis set for Li and K are shown in Table 3 and Table 4 respectively.

```
BASIS "ao basis" PRINT
#BASIS SET: (7s,4p) -> [4s,3p]
Li    S
    36.8382000           0.0696686
     5.4817200           0.3813460
     1.1132700           0.6817020
Li    SP
     0.5402050          -0.2631270           0.1615460
     0.1022550           1.1433900           0.9156630
Li    SP
     0.0285650           1.0000000           1.0000000
Li    SP
     0.0074000           1.0000000           1.0000000
```

Table 3. Lithium Basis set 3-21^{++}G

```
BASIS "ao basis" PRINT
#BASIS SET: (13s,10p) -> [6s,5p]
K    S
  1721.1755000           0.0648747
   260.0163300           0.3808593
    56.6245540           0.6773681
K    SP
    71.5572000          -0.1093429           0.1339654
    15.4389400           0.1130640           0.5302673
     4.4745510           0.9462575           0.5117992
K    SP
     4.1212750          -0.2699730           0.01994922
     1.1886210           0.3646323           0.43402130
     0.3756740           0.8107533           0.64532260
K    SP
     0.2445770          -0.2688250           0.0003081035
     0.0389720           1.1289830           0.9998787
K    SP
     0.0160630           1.0000000           1.0000000
K    SP
     0.0047000           1.0000000           1.0000000
```

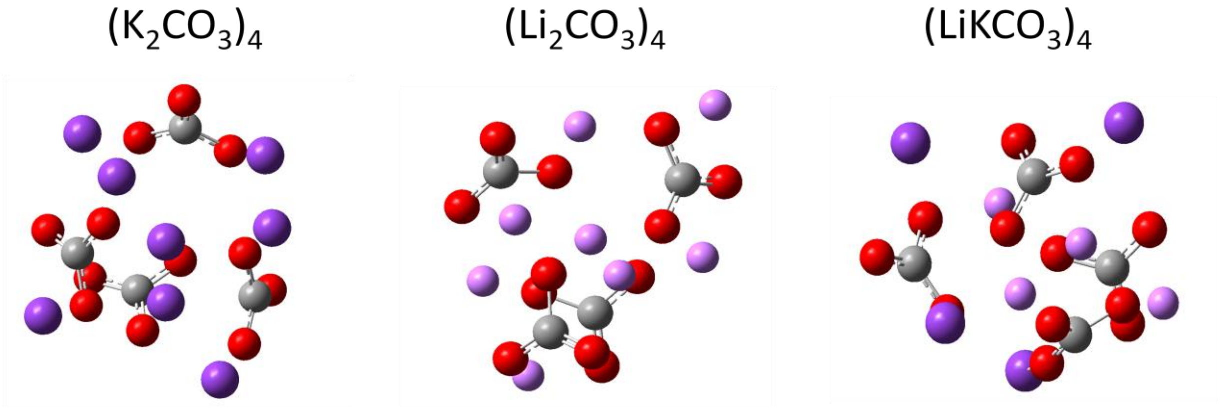
Table 4. Potassium Basis set 3-21^{++}G

2.2 Cluster Model

The interaction of individual oxygen with carbonate will be studied as combinations of different clusters shown in table 5, while different carbonates are studied using $(K_2CO_3)_4$, $(Li_2CO_3)_4$ and $(LiKCO_3)_4$ as simplest models (shown in Figure 3)

Table 5: Cluster Models of Oxygen and Carbonate

Structure	Formula			
Oxygen	O_2	O_2^-	O_2^{2-}	O^{2-}
Carbonate	CO_3^{2-}			
Carbonate	CO_5^{2-}	CO_5^{3-}	CO_5^{4-}	CO_4^{4-}



$(K_2CO_3)_4$ $(Li_2CO_3)_4$ $(LiKCO_3)_4$

Figure 3: Cluster Models of Carbonates

2.3 Geometry Optimization & Frequency Calculation

Each gas molecule: O, O_2, CO_2, CO_3^{2-} , CO_4^{2-} and CO_5^{2-} were optimized using the previous basis sets in order to calculate energy, electron distribution and bond distance. The energy is calculated simultaneously with geometry optimization calculations. Geometry optimizations attempt to find the lowest energy point on the surface. This is a state of equilibrium where the molecule is at its most stable state. It is also most likely to be found in nature at this state. Once the structure is input, the calculation begins and the energy is computed. Once the lowest energy point is located, a structure along with the total energy of the optimized molecule is obtained. The electron distribution and bond distance is also calculated. Frequency calculations must be carried out for the molecules because energy and geometry optimizations does not account for the presence of vibrations. Frequency calculations depend on the second derivative of the energy while geometry optimizations depend on first derivative. Geometry optimizations were carried out for oxygen species and carbonates in order to obtain data regarding charge, bond distances and total energy. The same procedures were put into effect for the cluster models in order to calculate total energy, optimization of the structures and electron distribution. The optimized simple carbonate (CO_3^{2-}) was taken to start the cluster models. The calculations were performed and three compositions of molten carbonate were produced. Additionally each complex with an assigned net charge of 0, -1 or -2 gathered information about the electrochemical process between oxygen and carbonate. If the oxygen atom still maintained a negative charge upon binding to carbon, this shows that there is a partial reduction of oxygen upon binding to carbon.

2.4 Software & Hardware

John Pople, was the clever creator of Gaussian09, a useful and powerful computational software program that is used to run calculations for all of the work mentioned in this study. It is capable of performing ab initio, density functional molecular orbitals and semi empirical calculations. All 3-D models were built using the graphical user interface GaussView. Four octa-core processors along with 64 GB of DDR3 memory were used to perform all calculations.

3. Results & Discussion

The following sections report the results that were calculated such as geometric optimizations, properties and the energy of each molecule.

3.1 Oxygen Species

The four oxygen species are shown in figure 4. The bond distance, total energy, and charges were obtained from the geometry optimization of four forms of oxygen (molecular oxygen, superoxide, peroxide and oxygen ion). The bond distance increases from 1.215 Å to 1.618 Å . The species were optimized with basis set 6-31G(d).

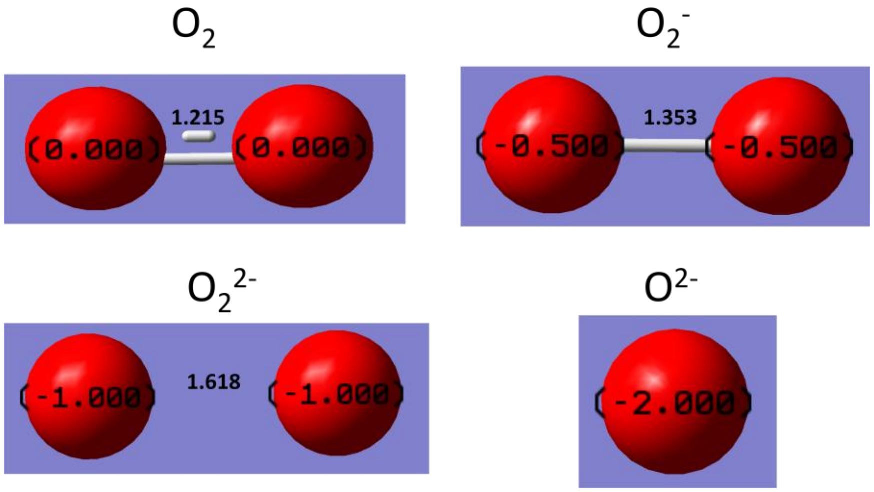


Figure 4: Oxygen Species B3LYP/6-31G(d)

According to Fig. 4, it is evident that as electrons were added to the structure, the bond distance increased from 1.215 Å to 1.353 Å then to 1.618 Å, which eventually broke the O-O bond, resulting in the product of two oxygen ions. This is known as the oxygen reduction reaction (ORR), shown in Eq. 3 below.

$$O_{2\,(g)} \rightarrow O_{2\,(ad)} \rightarrow O_2^{-}{}_{(ad)} \rightarrow O_2^{2-}{}_{(ad)} \rightarrow 2O^{2-}{}_{(ad)} \qquad \text{(Eq. 3)}$$

The breaking of the O-O bond can also be explained by molecular orbitals. As electrons were introduced into the orbitals of the oxygen species, they flow into anti-bonding molecular orbitals because these orbitals had room for extra electrons. Once the anti-bonding molecular orbitals was filled, the bond starts breaking and forming two ions which are needed for fuel cell operation. The Molecular orbital diagram is shown below in figure 5. Also shown in figure 5 are the MOs of oxygen which are sigma single bonds, pi double bonds and anti-bonding characteristics.

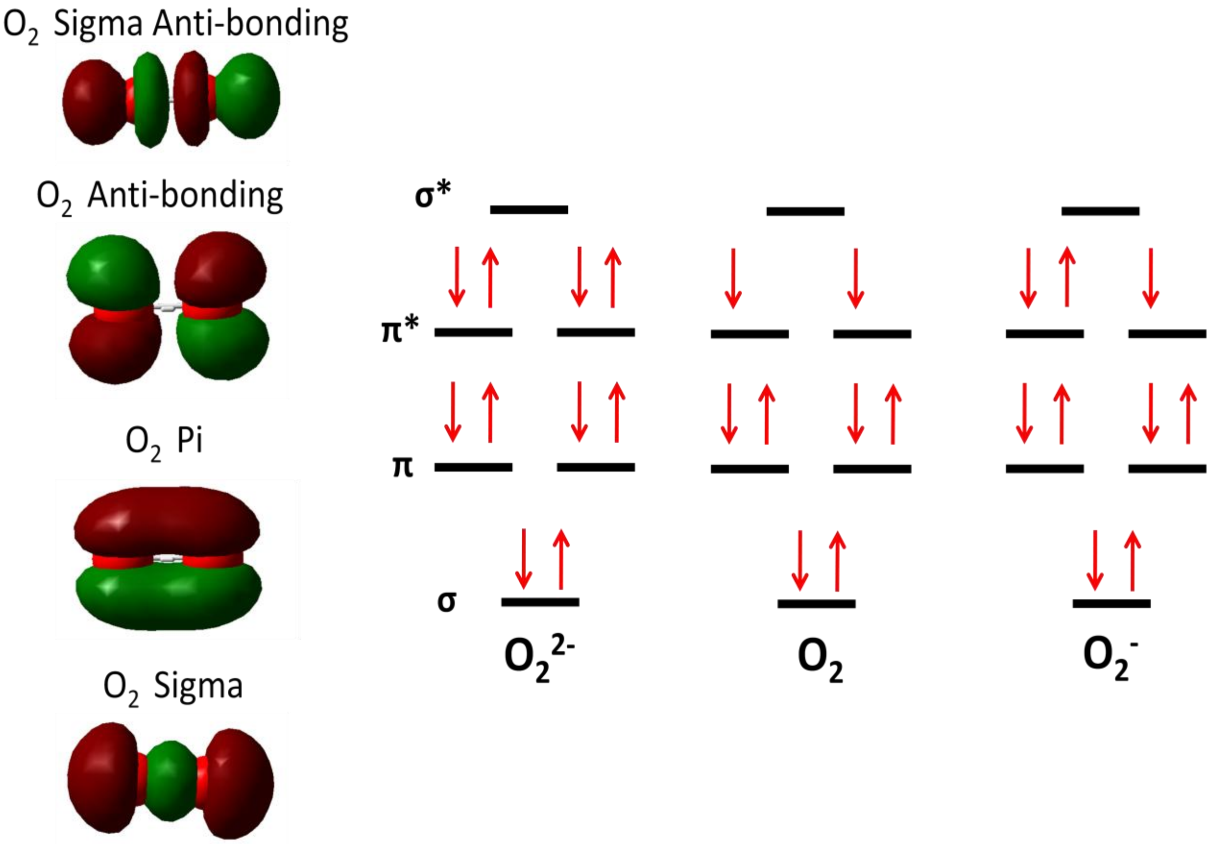
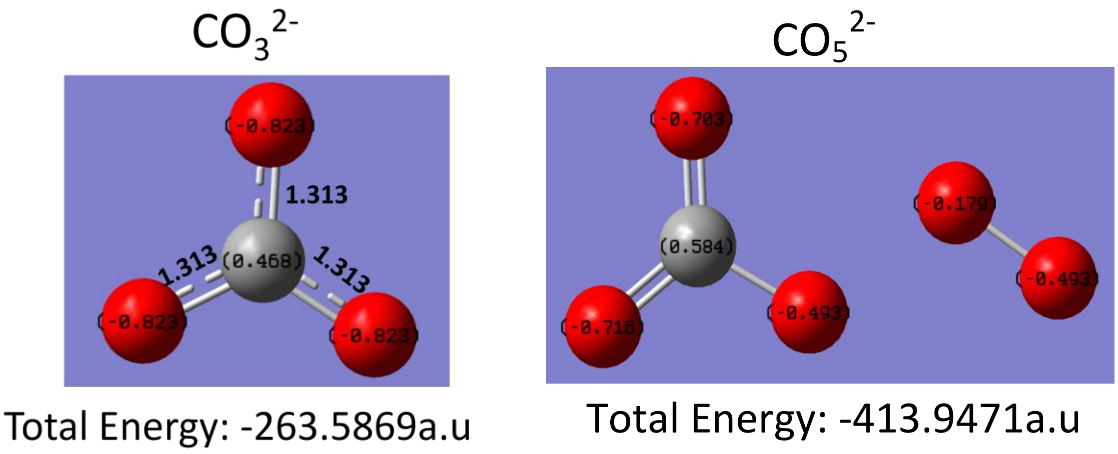


Figure 5: Molecular Orbitals and Electron Configurations of Oxygen Species

3.2 Carbonate

Carbonate structures were built and ran in order to calculate charge distribution, bond distance and total energy as shown in figure 6. CO_3^{2-} has a strong C-O bond distance of 1.313 Å and a total energy of -263.5869 au. The Oxygen atoms hold a negative charge while Carbon atom is positive because oxygen is the more electronegative atom, allowing it to attract the electrons. When this structure is combined with molecular oxygen, a stable complex, CO_5^{2-} is formed. The C-O bond closest to the oxygen molecule increased, proving that there is a chemical interaction between oxygen and carbonate. Yet the other two C-O bond distances decreased indicating that the bond strengthened, proving CO_5^{2-} to be a stable structure. The total charge of O-O is –0.672e⁻ , indicating that there is a partial reduction of oxygen upon binding to carbonate. The binding energy was calculated to be 105.3 kJ/mol by the equation,

$$BE = E_{oxygen/carbonate} - E_{oxygen} - E_{carbonate} \qquad \text{(Eq. 4)}$$

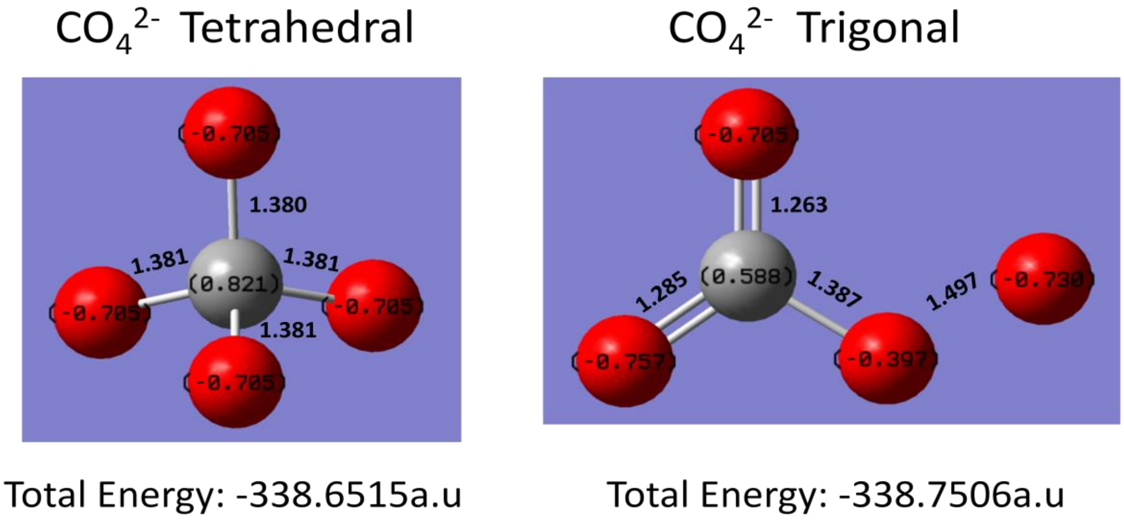


CO_3^{2-} Total Energy: -263.5869a.u

CO_5^{2-} Total Energy: -413.9471a.u

Figure 6A. Carbonate Complexes B3LYP/6-31G(d)

Two structures for CO_4^{2-} were optimized, trigonal and tetrahedral, as shown previously in figure 6B. The trigonal structure is 260 kJ/ mol lower in energy than the tetrahedral one, meaning that it is more stable. The calculated enthalpy change of $2CO_3^{2-} + O_2 \rightarrow 2\ CO_4^{2-}$ is -19.4 kJ/mol, implying CO_4^{2-} as a likely intermediate. The C-O bond distance also decreased from the trigonal to tetrahedral structure indicating that it is a stable structure.


CO_4^{2-} Tetrahedral

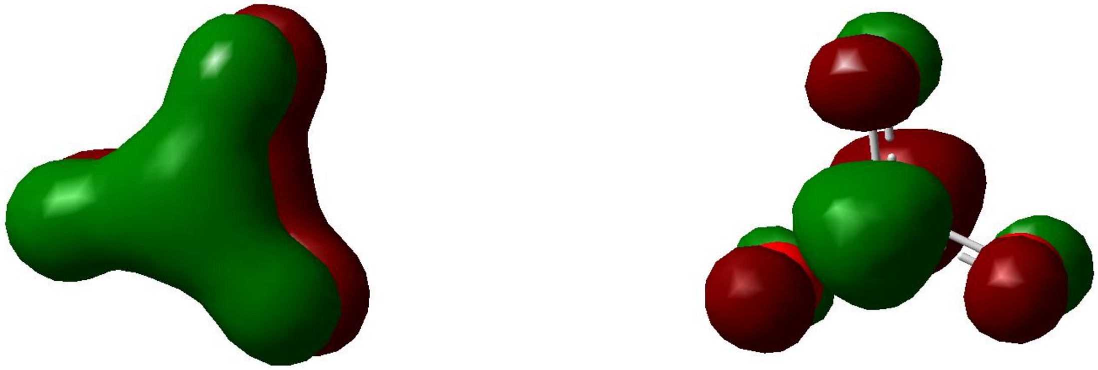
CO_4^{2-} Trigonal

Total Energy: -338.6515a.u

Total Energy: -338.7506a.u

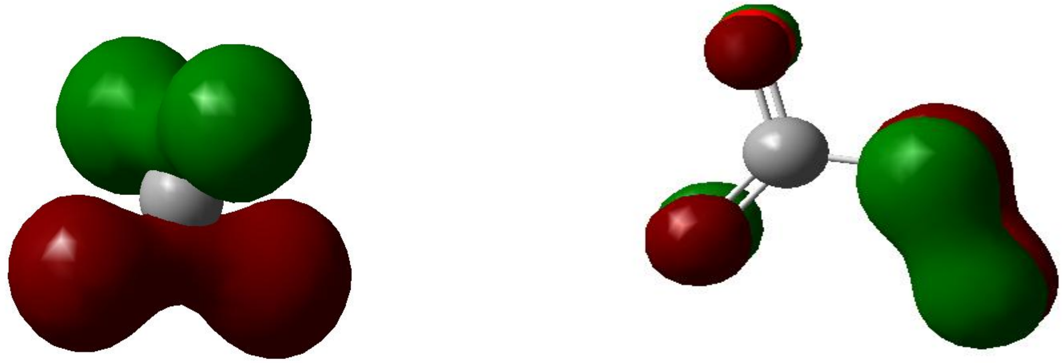
Figure 6B. Carbonate Complexes B3LYP/6-31G(d)

The molecular orbital structures are shown in figure 7. Picture A and B show strong π bonding and anti-bonding between the carbon and oxygen atoms respectively. Picture C shows strong π bonding as well but the overall bond distance is still very long and weak allowing the O_2 to be separated. Pictures D is the MO of CO_4^{2-} tetrahedral and trigonal. Tetrahedral shows mainly sigma bonding while the trigonal structure shows strong pi bonding on oxygen-carbon chain.



A. Pi

B. Anti-bonding



C. Sigma bonding

D. Oxygen bonding

Figure 7: Selected Molecular Orbitals of CO_3^{2-} and CO_4^{2-}

3.3 Lithium/Potassium Carbonate

Three compositions of molten carbonate were built using the GaussView interface and optimized as aforementioned. The total bond distance of oxygen to carbonate was calculated along with the bond distance of oxygen to lithium and potassium for each structure as shown previously in table 6. These values were averaged in order to check for consistency amongst the cluster models. The average O-C bond distance was 1.3245 Å for Lithium carbonate, 1.3248

Å for Potassium carbonate and 1.3227 Å for Lithium-Potassium carbonate. The average O-Li bond distance for Lithium carbonate was 1.8848 Å and 1.9047 Å for Lithium-Potassium carbonate. The average O-K bond distance was 2.6158 Å for Potassium carbonate and 2.6602 Å for Lithium-Potassium carbonate. These values are not only consistent with one another but when compared with previous research, are close to the same value. Previous research reported an average O-C bond distance as 1.2843 Å, an average O-Li bond distance as 1.9947 Å and an average O-K bond distance as 2.7833 Å for the Lithium-Potassium carbonate. These results show that either model composition of molten carbonate could be a possible enhancement to the ORR in solid oxide fuel cells. In addition to average bond distance, average charge was determined for each structure after two electrons were added to the structures. After electron addition the charge on lithium and potassium was reduced while the average charge of carbonate was increased. This indicates that electron distribution favors the carbonate. These values are reflected below in table 7.

Table 7. Calculated Charges on Ions of Molten Carbonate

Structure	$(K_2CO_3)_4$	$(K_2CO_3)_4^-$	$(K_2CO_3)_4^{2-}$	$(Li_2CO_3)_4$	$(Li_2CO_3)_4^-$	$(Li_2CO_3)_4^{2-}$	$(LiKCO_3)_4$	$(LiKCO_3)_4^-$	$(LiKCO_3)_4^{2-}$
Li	--	--	--	0.4473	0.2780	0.1525	0.2823	0.0565	0.0181
K	0.6820	0.4540	0.3276	--	--	--	0.7813	0.2890	0.4008
CO_3	-1.1645	-1.1578	-1.1550	-0.4123	-0.8168	-0.8050	-0.9428	-0.9398	-0.9375

4. Conclusion

In this project, we found that there is a strong interaction between oxygen and carbonate. By examining stable complexes such as CO_4^{2-} and CO_5^{2-} we were able to better understand the mechanism behind the ORR and can conclude that they promote the ORR in SOFCs. Calculated bond distances and binding energies show strong chemical interactions between oxygen and carbonate. We can also conclude that $(K_2CO_3)_4$, $(Li_2CO_3)_4$ and $(LiKCO_3)_4$ are simplest and suitable cluster models that will aid in modeling ORR in SOFCs with the presence of molten carbonate.

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