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Determination of Gibbs Free Energy in the Compound Formation of Li-P and Li-Fe-O by Pymatgen

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Abstract
The Gibbs free energy of the compound formation from a phase diagram based on Python Materials Genomic (Pymatgen) and Application Programming Interface (API) Key had been determined. The compounds shown were stable synthesized from the combination of Li-P and Li-Fe-O atoms. This stability was indicated by the value of the Gibbs free energy of the compounds formation obtained from the phase diagram of each atomic combination. The diagram was created from the integration between Python and the database from the Materials Project via an API Key using Pymatgen. From the research conducted for the combination of Li-P atoms, compounds and the Gibbs free energy of formation shown were Li_3 P (-0.697 eV/atom), LiP (-0.523 eV/atom), Li_3P_7 (-0.36 eV/atom), and LiP_7 (-0.159 eV/atom). For Li-Fe-O combination, the compound and the energy were Li_5 FeO_4 (-2.117 eV/atom), $LiFeO_2$ (-2.072 eV/atom), LiO_2 (-2.067 eV/atom), Li_2 FeO_2 (-1.979 eV/atom), Li_2 FeO_3 (-1.965 eV/atom), Fe_2O_3 (-1.907 eV/atom), Fe_3O_4 (-1.858 eV/atom), FeO (-1.728 eV/atom), Li_2O_2 (-1.651 eV/atom), and LiO_8 (-0.414 eV/atom). The most stable compound from each formation was the compound with the lowest Gibbs energy, i.e Li_3P and Li_5FeO_4.
Keywords: API Key; Gibbs free energy; Li-Fe-O; Li-P; pymatgen

Introduction

The substantial point in materials forming research is related to the energy that is required in forming materials. This quantity is known as the Gibbs free energy of compound formation. The Gibbs free energy of compound formation should satisfy a certain value so that the compounds are not easily reactive when used in normal conditions and they are still useful on a particular time scale. In the state that indicates the value of Gibbs free energy does not reach a certain value, the compound synthesized will easily corrode, decompose, polymerization, fire, or explode under environmental conditions of normal (Stull, D. R, 1971)

Modern science explains that at least three ways to determine Gibbs free energy of compound formation, there are by an experimental approach, mathematical approach with manual calculations, and computational or numerical method (Ong et al., 2012). The experimental approach using an apparatus in the laboratory. This method is widely used, but the instrument used is relatively large and these tools are not always available in the laboratory, and the value of Gibbs free energy of compound formation can only be obtained after the researcher doing the experiment so that the researcher requires physical raw materials to obtain the energy value for the formation of the synthesized compound (Taruminkeng et al., 2016). Determination of the Gibbs free energy of compound formation can be done experimentally by several methods (Kinoshita et al., 2019);(Morishita et al., 2020);(Morishita et al., 2012);(Yamasue et al., 2013). Another way to determine the Gibbs free energy of compound formation is a mathematical approach. The main constraint to this approach is the availability of information sources and supporting data, and calculations that relatively need a long time because they are done manually by researchers. This limitation can be overcome using a computational approach. By a computer-generated process, users need permission to access information sources regarding material-related data and determine what materials are used as raw materials for the formation of compounds. This computational approach requires a relatively fast time so that it is effective and does not require physical raw materials to obtain the energy values for the compound formation .

A computational approach that can be used to obtain Gibbs free energy of compound formation is pymatgen. Pymatgen or Python Materials Genomics is a programming library written in Python that can display scientific and statistical data, including Gibbs free energy of compound formation (Ong et al., 2012). This library can be downloaded for free on the http://materialsproject.github.com/pymatgen

page which is part of the Materials Project site, a collection of research data for materials studies (Jain et al., 2013). The Materials Project provides a wealth of physical and chemical data on materials, including lithium battery materials. Lithium is a battery material that is capable of reaching a charging cycle of up to 1000 cycles, meaning that it has a fairly high energy density (Mao et al., 2020);(Marom et al., 2011).

In the process of synthesizing lithium-ion batteries, several thermodynamic characteristics were obtained, including the Gibbs energy of compound formation (Popovich et al., 2021).Computational methods can be used to predict the stability of the compounds formed so that they can be used as references before experiments are carried out (S. Z. Wang et al., 2018). Elements that can bind to lithium to form battery material are phosphorus and iron. These two atoms have a good permittivity of the material so that it greatly affects the capacitance value of the battery material made (Mao et al., 2020);(Photos, 1989).

The process of forming this battery material also uses oxygen as an element so that electrons flow easily when the battery is used. The atomic combination that can be assigned is a combination of Li-P and Li-Fe-O. From this combination, solid ionic conducting compounds will be formed, if it gave a higher current until reaches a certain limit, the impedance or resistance in the compound will be lower so that the resulting battery material requires a relatively fast when charging power (Nazri, 1989).

These elements are reacted with the correct composition according to the mole part needed to synthesize certain compounds so that no raw materials are left in the reaction and the synthesized compound is more stable. Researchers can strive for the stability phase of a compound by paying attention to the composition of the material of the compound. The correct composition of the material can help to achieve the Gibbs free energy value for the formation of compounds that meet certain values (MacNeil et al., 2014).

Based on the description, this study was carried out to determine Gibbs free energy of compound formation from the bonding of lithium atoms with phosphorus, as well as the bonds of lithium atoms with iron and oxygen using pymatgen. The study started by making phase diagrams of Li-P and Li-Fe-O compounds using pymatgen to obtain the Gibbs free energy from the formation of these compounds. From this process, the composition of each element will be known so that the compound can be estimated to be stable. The determination of the Gibbs energy for the formation of these compounds has never been done before.

METHODS

Installing Pymatgen

Installing Pymatgen required the compiler (example: Google Colab) to write the installation commands. After we selected the compiler, the installation process could be done by writing "`pip install pymatgen`" then running the program. In this study, we did not need high hardware computer specifications. The hardware specifications in this study were Intel Core I3, 2 GB RAM, 500 GB HD.

Create a Phase diagram

Pymatgen use of special modules to create a phase diagram, there are `MPRester`, `MaterialsProjectCompatibility`, and `pymatgen.analysis.phase_diagram`. These modules must be written to the compiler. Pymatgen-based phase diagrams utilizing the big data in the Materials Project. To access the data, we needed a code known as an API Key. It was obtained from the page materialsproject.org/dashboard. We needed to write the following syntax after the API Key was obtained:

```
if __name__ == "__main__" :
    MAPI_KEY = "none"
    system = [ "X" , "Y" , "Z" ]
    mpr = MPRester(MAPI_KEY)
    compat =
    MaterialsProjectCompatibility()
```

by pasting the obtained *API Key* in none of the syntax and replacing X, Y, Z with Li-Fe-O and Li-P, then the specific commands in the process of creating a phase diagram could be done by writing the following syntax:

```
unprocessed_entries = mpr.get_
entries_in_ chemsys( system)

processed_entries = compat.
process_ entries(unprocessed_entries)

pd = PhaseDiagram(processed_entries)
plotter = PDPlotter(pd, show unstabl
e= False )
plotter.show()
    pda = "PDanalyzer(pd)"
    print("formula, materials_id)
    for e in pd.stable_entries :
 print ( "e.composition.reduced_
      formula, e.entry_id" )
 print ("formula, materials_id,e_
    above_hull(eV/atom), decomposesto")
    for e in pd.unstable_entries:
```

```
    e_above_hull =
    "pda.get_decomp_and_e_above
    _hull(e)"
print ("e.composition.reduced_
    formula, e.entry_id,
    e_above_hull, pretty decomp")
```

After all the syntax was written successfully, we could *run the program* to executed the commands. From this process, the phase diagram had been successfully made. Furthermore, the phase diagram that had been shown will present a diagram containing data from the value of the compound Gibbs free energy of formation or $Gf°$. This value could be seen by putting the mouse pointer over the circles in the resulting diagram.

RESULT AND DISCUSSION

Phase diagram

The first data obtained from this research is a diagram that provides a schematic of the phase stability of several constituent atoms as shown in Figure 1a and Figure 1b

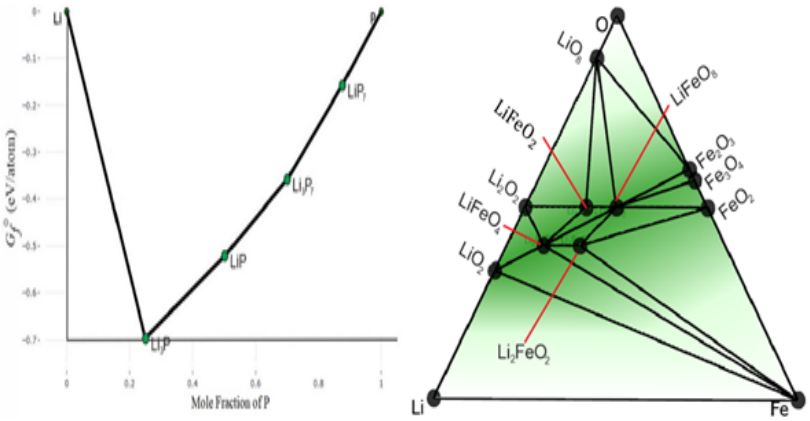
Figure1a is a phase diagram with Li-P elemental components showing several compounds that are probably stable from these two elements synthesized. The phase diagram with the two constituent components by pymatgen shown the composition of phosphorus. This value indicates the amount of phosphorus in each compound that allows stable synthesis. The curve presents the Gibbs free energy value of compound formation or $Gf°$ are lower for each material with a high phosphorus composition. That is, the composition of material will affect the value of $Gf°$ which is an indicator of the stability of the compound formed. Pymatgen featured several stable compounds synthesized from Li and P, such as Li_3P, LiP, Li_3P_7, and LiP_7.

Another phase diagram obtained from this study is shown in Figure 1b. This diagram is composed of three elemental components, there are Li, Fe, and O. The nets are shown in the diagram to interpret the composition of each component to form a stable compound. Pymatgen displays several stable compounds from the three atomic components, including Li_5FeO_4, $LiFeO_2$, LiO_2, Li_2FeO_2, Li_2FeO_3, Fe_2O_3, Fe_3O_4, FeO, Li_2O_2 and LiO_8.

Compound Gibbs free energy of formation

The Gibbs free energy of compound formation obtained from the diagrams shown in Figure 1a and Figure 1b, with the values of $Gf°$ shown in Table 1 and Table 2. The $Gf°$ values of the compounds that are possible to be stable formed from the combination of Li-P and Li-Fe-O atoms shown in Table 1 and Table 2 are the energy values possessed by these compounds when synthesized at 0 Kelvin and 0 atm. This state is almost impossible to achieve experimentally and only as a theoretical state. It is intended that the displayed $Gf°$ value can be used as a reference for other methods. If the $Gf°$ value of a compound shown another method less than the value shown pymatgen, then the energy of that compound is not sufficient to do the work. In other words, the compound formed is unstable.

Table 1 and Table 2 also show that the value of $Gf°$ is negative. This indicates that the reaction for the formation of compounds occurs spontaneously. This means that the process of compound formation occurs in a relatively fast time.



(a) Li-P phase diagram (b) Li-Fe-O phase diagram

Table 1: Gf° of Li-P as a constituent atom

Compound	Gf° **(eV/atom)**
Li_3P	-0.697 (mp-736)
LiP	-0.523 (mp-9588)
Li_3P_7	-0.36 (mp-28336)
LiP_7	-0.159 (mp-27687)

Table 2: Gf° of Li-Fe-O as constituent atoms

Compound	Gf° **(eV/atom)**
Li_5FeO_4	-2.117 (mp-19511)
$LiFeO_2$	-2.072 (mp-757614)
LiO_2	-2.067 (mp-1960)
Li_2FeO_2	-1.979 (mp-755094)
Li_2FeO_3	-1.965 (mp-774155)
Fe_2O_3	-1.907 (mp-19770)
Fe_3O_4	-1.858 (mp-19306)
FeO	-1.728 (mp-1279742)
Li_2O_2	-1.651 (mp-841)
LiO_8	-0.414 (mp-1235059)

The Gibbs free energy of some of the above compounds that listed in the reference are FeO (Gf°= -251.4 kJ/mol), Fe_2O_3 (Gf°= -742.2 kJ/mol), and Fe_3O_4 (Gf°= -1015.4 kJ/mol) (Engineering ToolBox, 2017). The compound formation was carried out at a temperature of $25^\circ C$ so that we could not directly compare it with the results obtained in this study due to different conditions.

CONCLUSION

Research of determination of Gibbs free energy in the compound formation of Li-P and Li-Fe-O has been successfully carried out by computational approach based on Python Materials Genomic (Pymatgen) and Application Programming Interface (API) Key. Pymatgen is a programming library written in Python that can display scientific and statistical data that can be downloaded for free on http://materialsproject.github.com/pymatgen. The atomic combinations simulated in this study were Li-P and Li-Fe-O. The most stable compound from each formation was the compound with the lowest Gibbs energy, i.e Li_3P and Li_5 FeO_4. This simulation can be used as a reference for conducting experiments in the future, where the Gibbs free energy results obtained from this method can be used as a reference to obtain stable compounds.

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