**CAMMP Week (10.06 - 15.06): Group 7**

**Problem 1**

**1.1 Introduction**

Our climate is rapidly changing and the global warming becomes an increasingly urgent problem. One of the major contributors for the global warming is the emissions of greenhouse gases, e.g. CO2 and NOx, by power generation and manufacturing industries etc. The development of new, low-emissions power generation technologies becomes significantly important. One such technology is the solid oxide fuel cell (SOFC), which is one of the most efficient and environmental-friendly technologies available for generating power from hydrogen, natural gas, biogas and other renewable fuels. Basically, a SOFC single cell t is composed of a dense electrolyte that is sandwiched by a porous cathode and a porous anode (Fig.1). It requires the fuel, such as hydrogen or natural gas, and oxidant reactants, such as oxygen or air to electrochemically react at high temperature and generate electrical energy.

我们的气候正在迅速变化，全球变暖成为一个日益迫切的问题。 全球变暖的主要原因之一是温室气体的排放，例如 二氧化碳和氮氧化物，通过发电和制造业等。新的低排放发电技术的发展变得非常重要。 一种这样的技术是固体氧化物燃料电池（SOFC），其是可用于从氢气，天然气，沼气和其他可再生燃料发电的最有效和环境友好的技术之一。 基本上，SOFC单电池t由致密电解质组成，其由多孔阴极和多孔阳极夹在中间（图1）。 它需要诸如氢气或天然气的燃料和氧气或空气等氧化剂反应物在高温下进行电化学反应并产生电能。

**O2-**

**O2-**

**O2-**

**Fuel**

**(e.g. H2 or CO or CH4)**

**Excess fuel & H2O, CO2**

**Air**

**(O2)**

**O2-**

**e-**

**e-**

**Cathode**

**Electrolyte**

**Anode**

Figure 1: Working principle of SOFC.

在操作期间，氧在阴极侧被还原成氧离子，氧离子随后通过电解质扩散到阳极。 阴极反应是：

将燃料（例如H 2，CO或CH 4）送入阳极，在那里将其氧化。 同时，产生电子。 因此，电流由外部电路中的电子流产生。 例如，如果将H2加入阳极，则阳极反应为：

因此，整个反应，如燃烧，产生水蒸气作为反应产物：

在这种情况下，可逆单元电位或理论开路电压可以通过能斯特方程计算：

During the operation, oxygen is reduced at the cathode side into oxygen ions that subsequently diffuse through the electrolyte to the anode. The cathode reaction is:

Fuel (e.g. H2, CO or CH4) is fed to the anode, where it is oxidized. Simultaneously, electrons are generated. The electricity is, thus, produced by the flow of electrons in the external circuit. As an example, if H2 is fed to the anode, then the anode reaction is:

Thus, the overall reaction, like combustion, yields water vapor as reaction product:

In this case, the reversible cell potential or the theoretical open circuit voltage, , can be calculated by the Nernst equation:

Where n is the number of electrons (n=4 in this case) that transfers during the reaction (in mole), is the standard reversible cell potential which can be calculated from , F is the Faraday constant (F=96485 C mol-1), is the ideal gas constant (R=8.314 J mol-1 K-1), and is the temperature in K. If the cathode gas is air (i.e. pO2=0.21 bar) and anode gas is 3% H2O humidified hydrogen (i.e. pH2O=0.03 bar and pH2=0.97 bar), then at 800 °C, when H2O(g) is the reaction product, the reversible cell potential of an SOFC single cell is about 1.1 V. The real potential of the cell is reduced when the current is drawn due to the different polarizations. To obtain higher voltage, the SOFC single cells are connected by interconnects in series and constructed into a stack.

其中n是在反应过程中转移的电子数（在这种情况下n = 4）（以摩尔计），是可以计算的标准可逆电池电位，F是法拉第常数（F = 96485 C mol-1） ），是理想气体常数（R = 8.314 J mol-1 K-1），是K的温度。如果阴极气体是空气（即pO2 = 0.21 bar），阳极气体是3％H2O加湿氢气（ 即pH2O = 0.03巴，pH2 = 0.97巴），然后在800℃，当H2O（g）是反应产物时，SOFC单电池的可逆电池电位约为1.1V。电池的实际电位降低 当由于不同的极化而绘制电流时。 为了获得更高的电压，SOFC单电池通过串联互连连接并构造成堆叠。

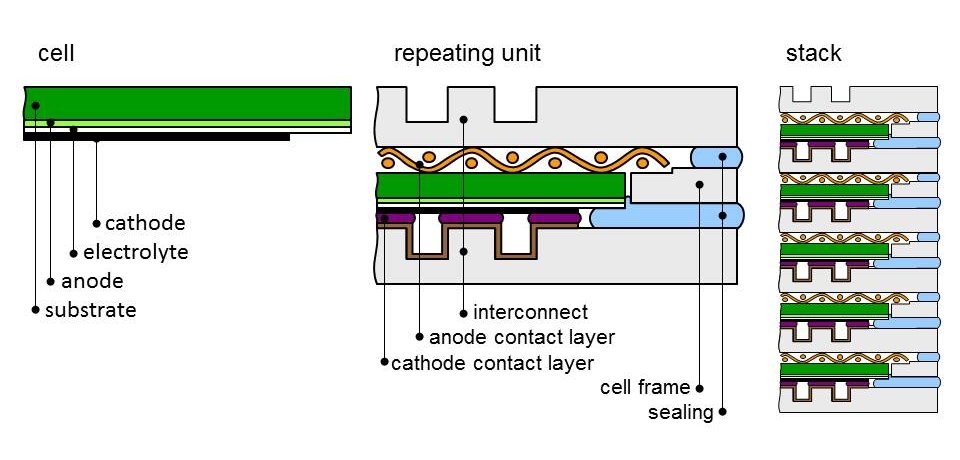


Figure 2: Construction of SOFC stacks.

In SOFC stacks, chromium containing steels, e.g. Crofer® 22 APU, are representative candidates of interconnect materials. During operation, a Cr2O3 containing scale forms on the metallic interconnect and leads to the evaporation of gaseous Cr species (e.g. CrO3 or CrO2(OH)2) from this scale. (La,Sr)(Co,Fe)O3-δ (LSCF) is a state-of-art cathode material. Sr is a reactive element in the LSCF cathode. As shown in Fig. 3, Sr tends to segregate out from the LSCF cathode in the form of SrO and becomes a reaction partner of volatile Cr species. The reaction will produce Sr-Cr-O secondary phases that can block the area for oxygen reduction, and subsequently leads to pronounced performance degradation of the SOFC.

在SOFC堆中，含铬钢，例如 Crofer®22APU是互连材料的代表性候选者。 在操作过程中，在金属互连上形成含Cr 2 O 3的氧化皮，并导致气态Cr物质（例如CrO 3或CrO 2（OH）2）从该氧化皮中蒸发。 （La，Sr）（Co，Fe）O3-（LSCF）是现有技术的阴极材料。 Sr是LSCF阴极中的电抗元素。 如图3所示，Sr倾向于以SrO的形式从LSCF阴极偏析出来并成为挥发性Cr物质的反应配偶体。 该反应将产生Sr-Cr-O第二相，其可以阻止氧还原的区域，并且随后导致SOFC的显着性能降低。

**Interconnect: Cr2O3-forming alloy**

**gaseous Cr species**

Sr/SrO

**Sr-Cr-O**

**Cathode: (La,Sr)(Co,Fe)O3-δ**

**Electrolyte: 8mol% Y2O3-ZrO2 (8YSZ)**

**Anode: Ni-YSZ**

Figure 3: Cr-poisoning of LSCF cathode.

If the cathode gas is dry air, then CrO3 will be the dominant gaseous Cr species. The possible reactions between the segregated SrO and CrO3(g) are:

如果阴极气体是干燥空气，那么CrO3将是主要的气态Cr物质。 分离的SrO和CrO3（g）之间可能的反应是：

If the temperature is fixed as 700 °C, these 4 reactions are dependent on partial pressure of CrO3 (pCrO3) and local oxygen partial pressure (pO2) in the cathode. With the given pCrO3 and pO2, **if SrO reacts with CrO3(g)**, then we **say the cathode is poisoned** by the Cr (Cr-poisoning of LSCF cathode). With the given pCrO3 and pO2, if SrO doesn’t react with CrO3(g), then we say our LSCF cathode is not poisoned.

如果温度固定为700℃，这4个反应取决于CrO3的分压（pCrO3）和阴极中的局部氧分压（pO2）。 对于给定的pCrO3和pO2，如果SrO与CrO3（g）反应，那么我们说阴极被Cr中毒（LSCF阴极的Cr中毒）。 对于给定的pCrO3和pO2，如果SrO不与CrO3（g）反应，那么我们说我们的LSCF阴极没有中毒。

**1.2 Task**

Based on the given data (**Cr-poisoning.xlsx**), solving the following two classification problems:

1) Whether the cathode is poisoned by Cr or not.

2) Classify different poisoning products.

1.2任务

根据给定的数据（Cr-poisoning.xlsx），解决以下两个分类问题：

1）阴极是否被Cr中毒。

2）对不同的中毒产品进行分类。

**Problem 2**

**2.1 Introduction**

Gibbs free energy (G) is one of the thermodynamic potentials. At constant temperature and pressure, the G of a system is the sum of the chemical potential of it constituents. For a system, if we know the **G as a function of composition at various temperature**, then using them, we can construct the phase diagram. Phase diagrams are a concise way to indicate the stable phases in any system. For example, the Fe-C phase diagram (Fig.4). The x-axis is the mass percentage of carbon, the y-axis is the temperature. If the mass percentage of carbon is 0.5% and temperature is 1000 °C, then Austenite (γ-Fe) will be the stable phase.

吉布斯自由能（G）是热力学势之一。 在恒定的温度和压力下，系统的G是其成分的化学势的总和。 对于一个系统，如果我们知道G在不同温度下作为成分的函数，那么使用它们，我们就可以构建相图。 相图是指示任何系统中稳定阶段的简明方法。 例如，Fe-C相图（图4）。 x轴是碳的质量百分比，y轴是温度。 如果碳的质量百分比为0.5％且温度为1000℃，则奥氏体（-Fe）将是稳定相。

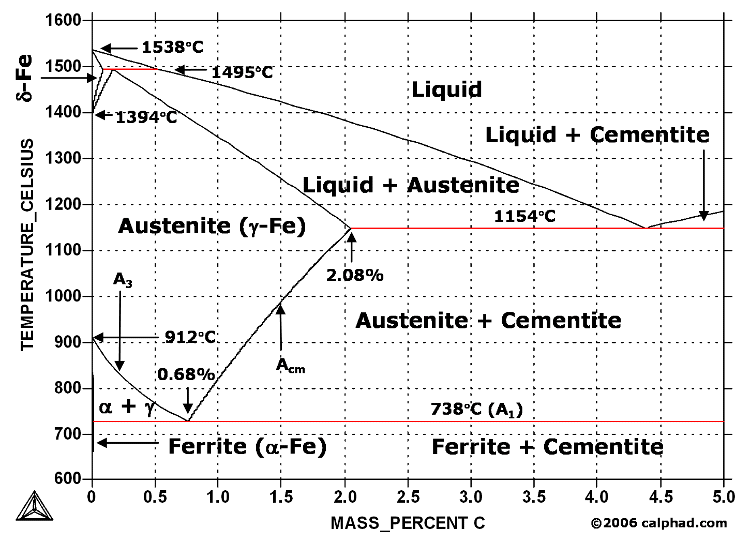


Figure 4: Fe-C phase diagram

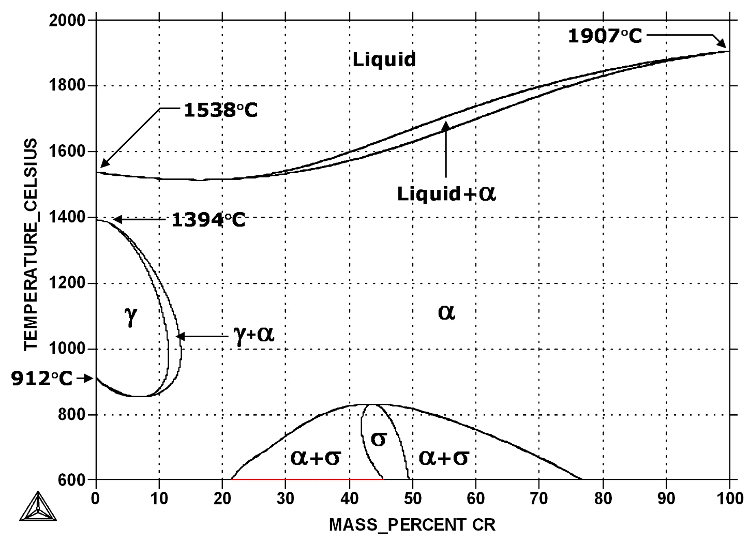


Figure 5: Fe-Cr phase diagram

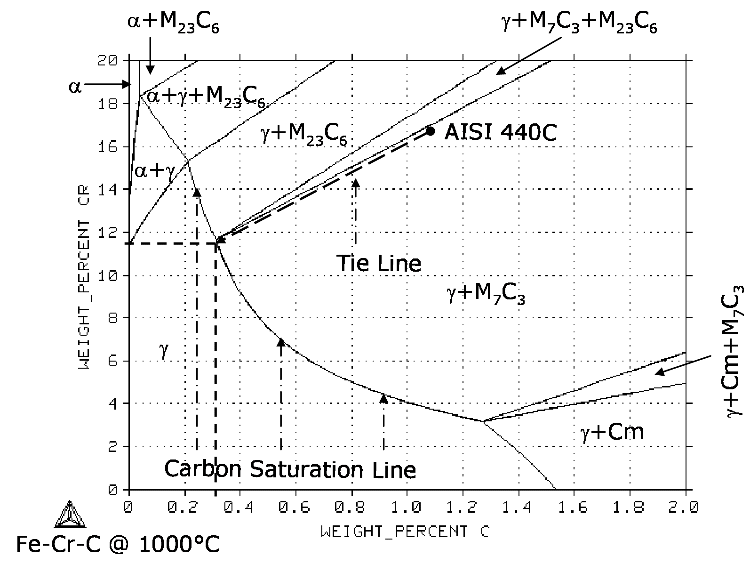


Figure 6: Fe-Cr-C phase diagram at 1000°C

**2.2 Task**

Is it possible to train a machine learning algorithm with the data (wt.-% of C, T and Gibbs free energy) of Fe-C system and the data (wt.-% of Cr, T and Gibbs free energy) of Fe-Cr system, then using the trained model to predict Gibbs free energy of Fe-C-Cr system by given wt.-% of C, wt.-% of Cr and T? (You can find prepared data in **Gibbs energy inference.xlsx**)

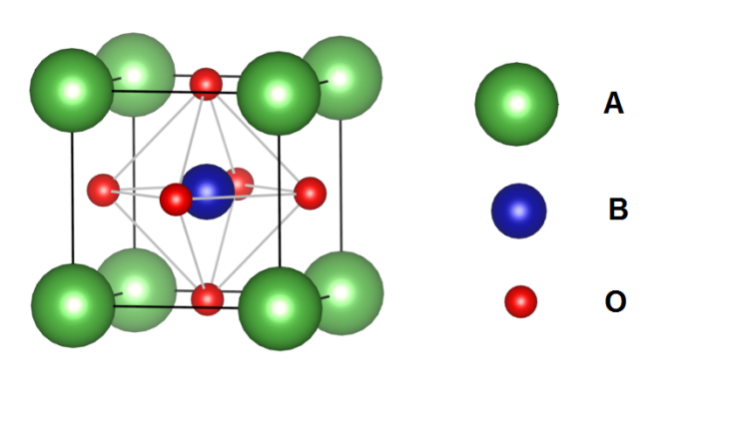
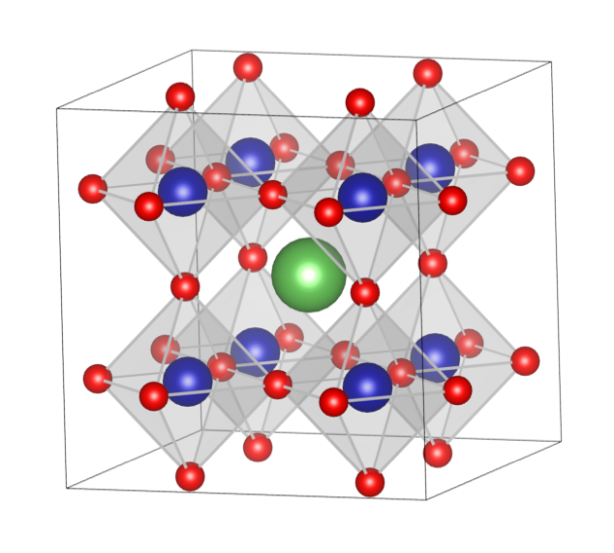
是否有可能用Fe-C系统的数据（C，T和吉布斯自由能的重量％）和铁的数据（Cr，T和吉布斯自由能的重量％）训练机器学习算法 -Cr系统，然后使用训练的模型来预测Fe-C-Cr系统的吉布斯自由能，给定重量％的C，重量％的Cr和T？ （您可以在Gibbs energy inference.xlsx中找到准备好的数据）

**Problem 3 (optional)**

**3.1 Introduction**

**Perovskite oxides** are promising candidates for the **cathode materials** in Solid Oxide Fuel Cells (SOFCs). The chemical formula of a typical perovskite oxide is **ABO3**, where A is the larger cation and B is the smaller cation. The ideal structure of perovskite oxide has a cubic symmetry. It can be viewed either as corner-sharing A-site cations with B-site cations at the center of cubic (Fig. 7a) or corner-sharing BO6 octahedral with A-site cations located in twelve-coordinated interstices (Fig. 7b). For most of the perovskite oxides applied as cathode in SOFCs, the A-site cation is a mixture of rare earth and alkaline earth atoms (such as La and Sr, Ca or Ba), while the B-site cation is a reducible transition metal (such as Mn, Fe, Co, or Ni).

钙钛矿氧化物是固体氧化物燃料电池（SOFC）中阴极材料的有希望的候选者。 典型的钙钛矿氧化物的化学式为ABO3，其中A是较大的阳离子，B是较小的阳离子。 钙钛矿氧化物的理想结构具有立方对称性。 它可以被视为角落共享A位阳离子，在立方体中心具有B位阳离子（图7a）或角落共享BO6八面体，A位阳离子位于十二个配位空隙中（图7b）。 对于大部分用作SOFC阴极的钙钛矿氧化物，A位阳离子是稀土和碱土原子的混合物（如La和Sr，Ca或Ba），而B位阳离子是可还原的过渡金属。 （例如Mn，Fe，Co或Ni）。

(a) (b)

Figure 7: The cubic perovskite ABO3 with a) B cation at the center of the cell and b) corner-sharing BO6 octahedral with A cation located in 12-coordinated interstices.

图7：立方钙钛矿ABO3，其中a）B阳离子位于电池中心，b）角共享BO6八面体，A阳离子位于12-配位间隙中。

In SOFC application, O2 is reduced into O2- at cathode surface (e.g. (La,Sr)(Co,Fe)O3 cathode). Then the O2- will diffuse through the bulk cathode to the electrolyte. The **diffusion of O2- in bulk cathode is dependent on the oxygen vacancies** that generated in bulk cathode. Therefore, to be a potential cathode material, it should be easier to form oxygen vacancy, i.e. **lower oxygen vacancy formation energy** is expected. There are also other requirements for cathode material, e.g. sufficient porosity for rapid diffusion of molecular oxygen, mechanically and chemically compatible with other cell components, and good tolerance towards impurities in the surrounding atmosphere…

在SOFC应用中，O 2在阴极表面（例如（La，Sr）（Co，Fe）O 3阴极）还原成O 2 - 。 然后，O 2 - 将通过体阴极扩散到电解质中。 体阴极中O 2 - 的扩散取决于体阴极中产生的氧空位。 因此，作为潜在的阴极材料，应该更容易形成氧空位，即预期较低的氧空位形成能。 阴极材料还有其他要求，例如： 足够的孔隙度，可快速扩散分子氧，与其他细胞成分机械和化学相容，并对周围大气中的杂质具有良好的耐受性......

**(La,Sr)(Co,Fe)O3-δ (LSCF) perovskite oxide** has sufficient electronic conductivity, high oxygen ionic conductivity, and high catalytic activity for the O2 reduction reaction in temperature range from 600 °C to 800 °C. It is a promising cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFC). **By substituting Sr2+ for La3+ at A-sites** in La(Co,Fe)O3, in order to maintain electronic neutrality, the substitution of Sr ions must be compensated by one or both of the following ways: i) electronic compensation by oxidizing B3+ to B4+ and ii) ionic compensation by formation of oxygen vacancies. The ionic and electronic compensations occur simultaneously and compete with each other. The electro-neutrality condition is expressed as:

（La，Sr）（Co，Fe）O3-δ（LSCF）钙钛矿氧化物在600℃至800℃的温度范围内具有足够的电子传导性，高氧离子传导性和对O 2还原反应的高催化活性。 它是用于中温固体氧化物燃料电池（IT-SOFC）的有前途的阴极材料。 通过在La（Co，Fe）O3中的A位取代Sr2 +得到La3 +，为了保持电子中性，必须通过以下一种或两种方法补偿Sr离子的取代：i）通过氧化B3 +来电子补偿 B4 +和ii）通过形成氧空位来进行离子补偿。 离子和电子补偿同时发生并相互竞争。 电中性条件表示为：

(1)

Therefore, LSCF has mixed electronic and ionic conductivity. The oxygen reduction process therefore takes place at the LSCF cathode surface by producing oxygen ions and consuming electrons. The produced oxygen ions are then transported through the bulk LSCF cathode to the electrolyte, while the electrons are supplied from the current-collector.

因此，LSCF具有混合的电子和离子传导性。 因此，氧还原过程通过产生氧离子和消耗电子在LSCF阴极表面发生。 然后，产生的氧离子通过块状LSCF阴极传输到电解质，而电子从集电器供应。

An appropriate stoichiometry of LSCF should be chosen, to guarantee sufficient ionic and electronic conductivity and to have a matched thermal expansion coefficient (TEC) with the adjacent layers. A higher amount of Sr atoms instead of the trivalent La on A-sites increases the ionic and electronic conductivity and the surface change of oxygen, which can be explained by the larger number of oxygen vacancies and electronic holes. Meanwhile, with increasing of Fe content at the B-sites, the TEC of LSCF is reduced that can be matched with the Y2O3-ZrO2 electrolyte or the gadolinium-doped ceria oxide diffusion barrier layer. The composition La0.6Sr0.4Co0.2Fe0.8O3-δ or the composition with slightly A-site deficiency La0.58Sr0.4Co0.2Fe0.8O3-δ is preferentially applied as the cathode material in SOFCs. La0.6Sr0.4Co0.2Fe0.8O3-δ has the highest electronic conductivity with the peak value of 330 S cm-1 at 550 °C. The TEC of La0.6Sr0.4Co0.2Fe0.8O3-δ in the temperature range from 100 °C to 600 °C is about 15.3\*10-6 K-1, which is thermally compatible with the Gd0.9Ce0.1O2-δ diffusion barrier layer (αl = 13.4\*10-6 K-1). The stability and durability for LSCF cathode is one of the decisive factors for the SOFC performance. The degradations issues of LSCF cathode (e.g. Cr-poisoning) limits the lifetime and commercialization of SOFC. Therefore, we want to find new potential cathode materials. The potential cathode materials should meet some requirements, e.g. it should have low oxygen vacancy formation energy.

应选择适当的LSCF化学计量，以保证足够的离子和电子传导性，并与相邻层具有匹配的热膨胀系数（TEC）。更高量的Sr原子而不是A位上的三价La增加了离子和电子传导性以及氧的表面变化，这可以通过更大数量的氧空位和电子空穴来解释。同时，随着B位的Fe含量的增加，LSCF的TEC减少，可与Y2O3-ZrO2电解质或掺杂钆的氧化铈氧化物扩散阻挡层相匹配。组成La0.6Sr0.4Co0.2Fe0.8O3-δ或具有轻微A位缺陷La0.58Sr0.4Co0.2Fe0.8O3-δ的组合物优先用作SOFC中的阴极材料。 La0.6Sr0.4Co0.2Fe0.8O3-δ具有最高的电子传导率，在550℃时峰值为330Scm-1。 La0.6Sr0.4Co0.2Fe0.8O3-δ在100°C至600°C温度范围内的TEC约为15.3 \* 10-6 K-1，与Gd0.9Ce0.1O2-δ热相容扩散阻挡层（α1= 13.4×10-6K-1）。 LSCF阴极的稳定性和耐久性是SOFC性能的决定性因素之一。 LSCF阴极的降解问题（例如Cr中毒）限制了SOFC的寿命和商业化。因此，我们希望找到新的潜在阴极材料。潜在的阴极材料应满足一些要求，例如：它应具有低氧空位形成能。

**3.2 Task**

If we know the oxygen vacancy formation energy of AFeO3 perovskite and ACoO3 perovskite (A = element in periodic system), can we make a prediction of the oxygen vacancy formation energy of AxX1-x(Co, Fe)O3 perovskite?

**Hint:**

* You can find some information in the data (**2017 high throughout DFT calculations of formation energy stability and oxygen vacancy formation energy of ABO3 prerovskites.csv**) that generated by *A. A. Emery and C. Wolverton, Scientific Data, 4:170153, 201*.
* You should think about which features variables will be used.
* To validate and test your model, oxygen vacancy formation energies of some AxX1-x(Co, Fe)O3 perovskites are prepared (**E\_Vo\_dopedPerovskites.xlsx**)

如果我们知道AFeO3钙钛矿和ACoO3钙钛矿（A =周期系中的元素）的氧空位形成能，我们能预测AxX1-x（Co，Fe）O3钙钛矿的氧空位形成能吗？

暗示：

您可以在A. A. Emery和C. Wolverton，Scientific Data，4：170153,201产生的数据中找到一些信息（2017年，在整个DFT计算中，形成能量稳定性和ABO3 prerovskites.csv的氧空位形成能）。

您应该考虑将使用哪些功能变量。

为了验证和测试您的模型，准备了一些AxX1-x（Co，Fe）O3钙钛矿的氧空位形成能量（E\_Vo\_dopedPerovskites.xlsx）