First principles study of Cr poisoning in solid oxide fuel cell cathodes: Application to (La,Sr) CoO₃

Sridevi Krishnan a,b,d,*, Manoj K. Mahapatra c, Prabhakar Singh a,d, Rampi Ramprasad a,b

Abstract

Solid oxide fuel cell (SOFC) systems provide efficient and clean power. Chromium poisoning is known to deteriorate the performance of the SOFC cathodes such as La1-xSrCoO3 (LSCO) due to the formation of undesired products. We identify the reaction products when LSCO is in a CrO₃ and O₂ atmosphere using first principle thermodynamics, with the assumption that gas-phase CrO₃ is the Cr source. Our results correctly identify SrCrO₄ as the primary Cr poisoning product as observed in experiments and also provides temperature-pressure regimes under which Cr poisoning effects may be avoided.

Keywords:
Density functional theory
First principles thermodynamics
Solid oxide fuel cells
Cr poisoning

Solid oxide fuel cells (SOFC) are complex electrochemical systems offering an efficient and clean route for energy conversion. Typically, doped perovskite oxides such as La1-xSrMnO₃ (LSMO) [1–3] and La1-xSrCoO₃ (LSCO) derivatives [4–9] are widely used as cathode materials in SOFCs [10]. Generally, these cathodes undergo performance deterioration due to a Cr deposition process known as Cr poisoning [11–15]. The most dominant Cr deposition product is observed to be SrCrO₄ [16–19] for LSCO based cathodes. It is necessary to understand the conditions and compositions at which these compounds form. Here we present a systematic study of the reaction energetics between the LSCO cathodes and the representative Cr species at SOFC operating conditions and provide valuable insights into the Cr poisoning process.

The volatile Cr species in the SOFC atmosphere is at the core of the detrimental effects of Cr poisoning. It has been observed that the volatile Cr species strongly depends on the oxygen partial pressure and the water content in the environment. CrO₂, the most dominant vapor species over the Cr₂O₃ scale [17] in dry air, is chosen as the representative Cr species in this study.

First principles calculations offer a powerful route for the systematic study of such complex phenomena [20–25]. We study the bulk reaction thermodynamics between a set of reactants (i.e., LSCO and CrO₃) to find the thermodynamically favorable reaction pathway as a function of temperature (T) and CrO₃ partial pressure (Pₐ). We correctly identify the experimentally known dominant Cr deposition products, SrCrO₄ and Co₃O₄, thus validating our approach. Additionally, this method accomplishes the following: (1) It identifies the P-T conditions to avoid Cr-poisoning and (2) it offers a strategy for determining the reaction energetics in other related situations, e.g., Cr poisoning of LSMO, BSCF (Pr0.5Sr0.5Co1−xFexO3) [26] cathodes.

The crystal structure of La1−xSr0.5Co0.5Cr0.5O₃ undergoes a rhombohedral (x ≤ 0.55) to cubic (x > 0.55) transition with increasing Sr concentration [27]. Typically, higher concentration of Sr [28] (x = 0.4) is used in LSCO based cathodes. Therefore, in this study we chose the compound La0.5Sr0.5Co0.5Cr0.5O₄ (x = 0.5), which is cubic at the high operating temperature encountered in SOFCs [29,30]. A thermodynamically favorable reaction pathway is obtained by combining a linear programming method with first principles thermodynamics. Our approach assesses all possible products of a set of reactants and arrives at the energetically favorable set of products. The reaction free energy is then obtained from the newly created phase diagram at experimental P-T conditions.

For our particular reaction of interest (see Table 1), the element space defined by our reactants consists of La, Sr, Co, Cr and O. A product pool is then created comprising of all possible reaction products such as the elemental metal, binary oxides, ternary oxides

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Table 1

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Product pool</th>
</tr>
</thead>
<tbody>
<tr>
<td>La0.5Sr0.5CoO3, CrO3</td>
<td>La0.5Sr0.5CoO3, CrO3</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>Cr2O3</td>
</tr>
<tr>
<td>Cr3O4</td>
<td>Cr3O4</td>
</tr>
<tr>
<td>LaCoO3</td>
<td>LaCoO3</td>
</tr>
<tr>
<td>La2O3, SrO2, Co2O3, Cr2O3</td>
<td>La2O3, SrO2, Co2O3, Cr2O3</td>
</tr>
</tbody>
</table>

**Reaction**

\[
\begin{align*}
\La_{0.5} & \cdot \Sr_{0.5} \cdot \CrO3 \\
\pm & 2\CrO3 \rightarrow (\La + \Sr + \Cr + \CrO3 + \LaO2 + \SrO) + (\CrO3 + \CrO3) + \CrO3
\end{align*}
\]

\[
\Delta \mu_{\text{CrO3}}(T, p) = \Delta \mu_{\text{CrO3}}(T, p^0) + k_B T \ln \left( \frac{p_{\text{CrO3}}}{p^0_{\text{CrO3}}} \right)
\]

$$E_p = \min \left\{ \sum_{i=1}^{c_i} E_i + c_0, \ldots, 1) \mu_0 \right\}$$

$$E_p = \mu_0 - E_0, \quad \text{where } E_0 \text{ is the DFT energy of an isolated } \text{O}_2 \text{ molecule.}$$

$$\Delta \mu_0(T, p) = \Delta \mu_0(T, p^0) + k_B T \ln \left( \frac{p_{\text{CrO3}}}{p^0_{\text{CrO3}}} \right)$$

The thermodynamically favorable decomposition pathway.

The thermodynamically favorable decomposition pathway is obtained by minimizing Eq. (2) subject to the stoichiometry and oxygen including the chromates (Table 1). Thus, we now have a reaction (Eq. (1)) with a variable $x$ (concentration of CrO3) on the reactant side and coefficients $c_i$ preceding each of the products whose values are unknown. The thermodynamically favorable set of products can be obtained once the value for each of these coefficients has been solved as a function of $x$ values.

The linear programming (LP) method offers an efficient approach to find the most energetically favorable decomposition pathway for the reactions without explicitly identifying all possible reaction pathways and comparing them. The optimized energy of the products ($E_p$) of the reaction between $La_{0.5}Sr_{0.5}CoO_3 + xCrO_3$ is obtained by minimizing Eq. (2) subject to the stoichiometry preservation constraints in Eq. (4) in Table 1. Here again, the product energy $E_p$ depends on the oxygen chemical potential and assuming ideal gas behavior, it can be related to its partial pressure according to Eq. (3). The oxygen chemical potential ($\Delta \mu_{\text{O}_2}$) can be determined using statistical thermodynamics [25,31] or the JANAF data [32]. The oxygen partial pressure is fixed at 0.2 atm in accordance with the experimental SOFC conditions for all our calculations. Thus, in the calculation of free energy, the entropic contributions are included only for the gaseous species CrO3 and O2. The summation in Eq. (4) is done for each element in the element space (i.e., La, D, Mn, Cr and O). For example, in case of the element La, the variables $s'_1$ and $s''_1$ in Eq. (4) becomes $s'^1_1$ and $s'^2_1$ for the ith product in the pool. Then, $s'^1_1 = 0.5$ and $s'^2_1 = 2$, the proportion of La in the reactant $La_{0.5}Sr_{0.5}CoO_3$ and the 5th product $La_{2.5}O_3$ in the pool respectively (refer Table 1).

Then the free energy of the reaction (Eq. (1)) can be obtained as defined in Eq. (5) as a function of CrO3 chemical potential. Assuming ideal gas behavior, the CrO3 chemical potential can be related to its partial pressure according to Eq. (6). The CrO3 chemical potential ($\Delta \mu_{\text{CrO3}}$) can be determined using statistical thermodynamics [25,31] or the JANAF data [32]. The change in the concentration of CrO3 alters the reaction pathway which in turn affects the free energy of the reaction. We systematically study the reaction energetics between CrO3 and $La_{0.5}Sr_{0.5}CoO_3$ for a large number of CrO3 concentrations ($x$) ranging from 0 to 1 and the temperature from 800 to 1500 K from which the phase diagram is constructed. Although the reaction kinetics also plays a vital role, it is important to recognize that our approach provides decomposition pathways based solely on the reaction energetics.

All energies of the reactants and products are obtained from spin polarized calculations using DFT as implemented in the VASP [33,34] code. The exchange correlation is treated using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [35] functional. The projector augmented wave (PAW) potentials [36] were used to describe the core states. All calculations were performed with a cutoff energy of 520 eV and a Monkhorst-Pack k-point grid with a spacing of at least 0.13 Å⁻¹ was used to sample the Brillouin zone. The atomic positions were relaxed until the force on each atom fell below a threshold of 0.02 eV/Å. $La_{0.5}Sr_{0.5}CoO_3$ was relaxed in the cubic structure while the ground state structures were considered for the rest of the compounds. A shift of 1.38 eV/O2 molecule is used to destabilize the total energy of the O2 molecule (E02 (corrected) = - 8.48 eV) to account for the overbinding of the oxygen molecule in the GGA-PBE level of theory, consistent with previous results [37–39]. It is well known that the treatment based on the semilocal GGA functionals are insufficient for the highly correlated oxides considered here [40]. DFT + U is generally employed to overcome this issue however identifying an optimal value of U for the transition metals in different chemical environment is questionable [41]. Moreover, hybrid functionals are computationally expensive therefore we employ a consistent GGA-PBE level of theory across all products.

To understand the energetics of the different set of products with the CrO3 concentration, the free energy of the reaction ($F_k$ in Eq. (5)) between CrO3 and $La_{0.5}Sr_{0.5}CoO_3$ at 900 K is shown in Fig. 1(a). The color gradient represents the slope (value of $x$) of the lines. Colors from blue to red corresponds to $x$ values from 0 to 1, respectively. The lowest free energy at various $\Delta \mu_{\text{CrO3}}$, and their corresponding $x$ values are obtained for the temperature range of interest.

The $c_i$ values corresponding to the CrO3 concentration ($x$) of interest at 900 K is shown in Fig. 1(b). The columns without any bubble correspond to $c_i$ values of zero and the ones with the bubble correspond to the thermodynamically favorable product with the bubble sizes representing the amount of that product. It is imme-
Immediately evident that the reaction pathway is altered with increasing CrO$_3$ concentration ($\alpha$) values along with the change in the amounts of the products. It is clear that the La$_{0.5}$Sr$_{0.5}$CoO$_3$ is stable and remains undisturbed in the absence of Cr vapor ($\alpha = 0$). The Cr reaction products begin to appear with increasing concentrations of CrO$_3$. Interestingly, we find that the by-product of Cr poisoning, SrCrO$_4$, appears in the thermodynamic reaction pathway and the amount of the compound in the product increases with increasing $\alpha$ values. Although, the other Cr-Co compound CoCr$_2$O$_4$ is present in the product pool, it does not appear as a thermodynamically favorable product.

Based on the chemical potentials and the corresponding thermodynamically favorable products, the phase diagram of reaction for a range of experimentally observable temperature and CrO$_3$ partial pressures ($P_{CrO_3}$) (Fig. 2) is constructed. We have identified the window of experimental $P_{CrO_3}$-$T$ conditions based on the measurement of chromium evaporation rate in the SOFC atmosphere of different chromia forming alloys (the source of chromium) [17,42]. In this window of experimentally observed temperature and pressure (blue dotted rectangle in Fig. 2), the energetics of the interaction between La$_{0.5}$Sr$_{0.5}$CoO$_3$ and CrO$_3$ can be classified as the reactive and the non-reactive sections. In the reactive sections, the pathway for the reaction between CrO$_3$ and La$_{0.5}$Sr$_{0.5}$CoO$_3$ proceeds to form products such as Co$_3$O$_4$, SrCrO$_4$, LaCoO$_3$ and O$_2$ coexisting with the reactant, La$_{0.5}$Sr$_{0.5}$CoO$_3$ at experimental $P_{CrO_3}$-$T$ conditions. However, at low $P_{CrO_3}$ and high temperatures the LSCO compound remains unreacted (Fig. 2).

We find that for the stoichiometric LSCO, the thermodynamically favorable pathway includes the formation of the experimentally observed Cr poisoning products, SrCrO$_4$ and Co$_3$O$_4$. Our results show that the formation of SrCrO$_4$ is energetically favorable over the formation of CoCr$_2$O$_4$. This is in line with experimental observations where only SrCrO$_4$ [16] is observed as the Cr poisoning product, further validating our finding.

The formation of the Cr poisoning product SrCrO$_4$ in the reaction phase diagram (Fig. 2) determines the P-T conditions to avoid Cr poisoning effects. The Cr poisoning effects are dominant at the cathode surfaces, however, we focus on the bulk thermodynamics to determine the optimal Cr concentration which makes the Cr poisoning process possible. Thereby providing guidelines of the threshold Cr partial pressure to avoid the detrimental effects. Accordingly, at $\approx$900 K, the La$_{0.5}$Sr$_{0.5}$CoO$_3$ remains unreacted at low CrO$_3$ partial pressures ($< 10^{-3}$ atm), however, with increasing CrO$_3$ partial pressure, it readily reacts. On the other hand, with increasing temperature higher concentrations of CrO$_3$ are accommodated without reaction. For instance, at temperatures above $\approx$1050 K, LSCO remains unreacted even for a higher CrO$_3$ partial pressure of $\approx 10^{-8}$ atm. Therefore, our findings provide good guidelines for the experimental P-T range to avoid effects of Cr poisoning in LSCO.

The bulk reaction thermodynamics between La$_{0.5}$Sr$_{0.5}$CoO$_3$ and CrO$_3$ is studied for the thermodynamically favorable pathway.
employing first principles thermodynamics. The variation of CrO$_3$ in the reaction is mapped to the partial pressure of CrO$_2$ and the phase diagram of the reaction is extracted. We find that the CrO$_3$ concentration significantly alters the reaction products. We observe that the formation of the Cr poisoning by-product, SrCrO$_4$, is favored for a wide range of experimental CrO$_3$ partial pressures and temperatures agreeing with experimental observations. In addition, our study provides a prediction for experimental P-T conditions to avoid Cr poisoning effects in LSCO. This method can be extended to identify reaction energetics of other multicomponent systems as well.

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References

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