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Thermodynamics of LSM-YSZ Interfaces- A Revisit with Confirmed $\text{La}_2\text{Zr}_2\text{O}_7$ Thermodynamic Data

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Abstract

From late 1980's to early 90's, Yokokawa made a series of thermodynamic analyses on the perovskite electrode and the YSZ electrolyte. For the LSM-YSZ interface, evaluation of the thermodynamic data of $\text{La}_2\text{Zr}_2\text{O}_7$ was made so as to obtain consistency among LSM-YSZ diffusion couple experiment by Lau and Singhal, thermogravimetric results on nonstoichiometric $\text{La}_{1-x}\text{MnO}_3$ by Shimomura et al, and calorimetric measurements by *V. R. Korneev. After this compilation, a new calorimetric value determined by M. Bolech et al. was more negative than the compiled value. The calphad-type optimization was made by Gaukler's group with relying on the new value so that they criticized Yokokawa's evaluated data of $\text{La}_2\text{Zr}_2\text{O}_7$ and his analytical results of phase relations related with LSM-YSZ interface. Even so, Yokokawa's analyses relied on Lau and Singhal data so that the issue to be confirmed is which diffusion couple data by Lau and Singhal or calorimetric data by Bolech is incorrect. Upon Yokokawa's request, Navrotsky's group made calorimetric measurements again on $\text{La}_2\text{Zr}_2\text{O}_7$ and their new data indicate less negative. It becomes more consistent with diffusion couple data by Lau and Singhal. These chronological events eventually confirmed that Yokokawa's initial treatment is essentially valid.

Since Yokokawa's first work on the LSM-YSZ interface, many interesting and important experimental results have been reported not only for SOFC mode but also SOEC mode. These new findings will be discussed in terms of equilibrium data as well as some kinetic considerations. For the SOFC mode, the direct confirmation on Yokokawa's results was made by Siemens. Quite recently, Matsui et al reported the interesting features of slightly A-site deficient LSM cathodes having different La content, indicating the formation of a dense LSM layer at the LSM-YSZ interface more significantly for the La-rich composition, where the A-site deficiency becomes more significant with growing possibility of $\text{La}_2\text{Zr}_2\text{O}_7$ formation at a given A-site deficient value. Analogous consideration to the sintering behavior of the A-site deficient cathode on heat treatment suggests that the oxide ion vacancies formed during the electrochemical polarization together with the cation vacancies enhance the sintering of LSM cathode without precipitation of Mn oxides.

Behavior under the SOEC mode should depend largely on the magnitude of polarization, since the LSM-YSZ interface chemistry depends on the oxygen potential mainly because the A-site deficient width or the $\text{La}_2\text{Zr}_2\text{O}_7$ formation region depends on the valence of Manganese ions. With increasing oxygen potential, the $\text{La}_2\text{Zr}_2\text{O}_7$ is partially formed at the interface, and then finally $\text{La}_2\text{Zr}_2\text{O}_7$ as well as MnO_2 is formed as a result of oxidative decomposition.

1. Introduction

The lanthanum manganite electrode has been first utilized as stable cathodes in SOFC in the early stage of SOFC development which is recognized as the first generation cells (1). In particular, from late 1980s to early 1990s, many important investigations have been made to resolve the industrial issues (2,3). The most important issue associated with this cathode was the interaction between the YSZ electrolyte and the lanthanum manganite-based cathodes (1). In order to resolve this issue and related properties, Yokokawa *et al.* started the thermodynamic analyses on this issue by adopting the comprehensive evaluations of the thermodynamic properties of perovskite-type compounds (4,5) and also of the fluorite-type solid solutions (6,7), by making analyses on the thermodynamic stability of interfaces and also by comparing those results with industrial efforts of optimizing compositions of LaMnO₃-based cathodes (8,9). With satisfactory, those understandings are quite consistent to derive the essentials of materials science involved which range from the fundamental physicochemical aspects to the industrial efforts.

Recently there are growing interests in the LSM-based electrodes as anodes for SOECs (10) in addition to the continuous interests as cathodes for SOFCs (11). These recent investigations revealed new experimental results concerning the LSM-YSZ interface stability issues. Since the Yokokawa's thermodynamic analytical results are criticized as wrong by Gauckler's group who made a series of calphad-type optimization (12,13), the issues associated with the evaluation of thermodynamic data of La₂Zr₂O₇ are first reviewed from Yokokawa's point of view. Then, the thermodynamic characteristic features will be discussed in comparison with recent interesting features observed in SOFCs or SOECs.

2. Interface Stability and Thermodynamic Data of La₂Zr₂O₇

2.1 Yokokawa's efforts in establishing thermodynamic data and interface chemistry of LSM-YSZ.

Essential points of Yokokawa's approach on this issue can be summarized as follows;

(1) Proper treatment on multicomponent multiphase equilibria

Industrially important materials are frequently multicomponent substances; LSM is the perovskite-type compounds in the La-Sr-Mn-O system and sometimes Ca instead of Sr is adopted as dopant; YSZ is the fluorite-type solid solutions and exhibits dissolution of other cations in it. As a result, not only phase diagram calculations (14) or the construction of chemical potential diagrams (15) are used but also complicated chemical equilibrium calculations (16) are needed to confirm the equilibrium features among a plausible combination of cathodes and electrolyte.

(2) Resolution of interconsistency among various features associated with interface chemistry

First important experimental results are diffusion couple made by Lau and Singhal between LSM and YSZ (1), showing the formation of La₂Zr₂O₇ at the interface without precipitation of manganese oxides. This is apparently different from similar features for other combinations, for example, of LaCoO₃ and YSZ, exhibiting the formation of La₂Zr₂O₇ and CoO precipitation (17). The behavior of LSM-YSZ can be interpreted in terms of the A-site deficiency of LaMnO₃-based perovskites which was carefully observed by Shimomura *et al.* (18) (quoted by Mizusaki (19)) and also of the thermodynamic data of La₂Zr₂O₇ given by Korneev (20). As given in Table 1, Korneev's data is not consistent between their reported values for enthalpy changes for formation from elements and from constituent oxides. The value from the constituent

oxides did not give any reasonable results but the value from the elements provided excellent consistency among many different observations as described in the introduction. This gives Yokokawa strong confidence about this value so that he published as his evaluated (not estimated) data.

(3) Thermochemical consistency

Evaluation of thermodynamic (or thermochemical) data has been made in two different ways; one is focused on the thermochemical network among many elements and their compounds, the other being beginning with the phase relations in binary systems and then higher systems. The most important work in the former approach is the database created by NBS (currently NIST) (21); the thermodynamic database MALT (22) is based on those NBS data as primarily important data; Yokokawa is a member of the MALT group so that his evaluated/estimated data are adjusted for the NBS / MALT database.

Thus, Yokokawa published a series of papers concerning the LSM/YSZ interface stability (23). Furthermore, he extended analyses on comparison with industrial efforts by Westinghouse on SOFC, Dornier on SOEC and Mitsubishi Heavy Industries on SOFC (24).

2.2 Calorimetric Determination of Enthalpy of $\text{La}_2\text{Zr}_2\text{O}_7$ and Calphad-type evaluation of Phase Equilibria by Gauckler's group

After this thermodynamic analyses, the thermodynamic data of $\text{La}_2\text{Zr}_2\text{O}_7$ was measured by Bolech *et al.* (25) but this value was extremely more endothermic compared with the Yokokawa's adopted value (23) from the prior calorimetric work (20). Although this new calorimetric value gave impressions that it seems reliable because of usual high accuracy of calorimetric determination and subsequent *EMF* investigations (26,27) supported this value as listed in Table 1, Yokokawa did not change his value in the database, because his obtained consistency among many various investigations on thermodynamic properties, electrochemical properties (28) and diffusion couples (1) is quite excellent except for the new calorimetric value (25). However, evaluation based on the Calphad-type optimization relied on the calorimetric results, leading to a conclusion that Yokokawa's analytical results are wrong (12).

2.3 True Issue is inconsistency

Since Yokokawa knew that the true issue is not in his evaluation itself but in the consistency between the calorimetric value (25) and other properties to be considered, particularly, diffusion couple experiments between LSM and YSZ made by Lau and Singhal (1) which has been recognized as the most important experimental results but was not considered in the evaluation by Gauckler's group (12). Since the results by Lau and Singhal have been confirmed by many investigations, Yokokawa informed Navrotzky about this inconsistency with his doubt that her calorimetric value must be wrong. Upon his request, Navrotzky and colleague re-determined the calorimetric value (29).

2.4 Redetermination of Calorimetric Value of Enthalpy

Their new value is listed in table 1 indicating that this is about 20 kJ/mol more negative than that of Yokokawa's evaluated data and this difference decreases significantly from the initial difference, about 50 kJ/mol. Although there remains some difference, it is not so surprising when comparison is made even in the enthalpy data for LaMnO_3 (31,32). The data derived by Navrotsky's laboratory(30) is again more negative than Yokokawa's evaluated data (4) and also more negative than recent measured and evaluated value by Jacob and Attaluri(32).

Table 1. Experimental and Evaluated data for the Enthalpy changes for La₂Zr₂O₇ and LaMnO₃

authors	year	$\Delta_{f,\text{oxide}}H^\circ/\text{kJmol}^{-1}$	$\Delta_f H^\circ/\text{kJmol}^{-1}$	Method	ref
(a) La ₂ Zr ₂ O ₇					
V.R. Korneev	1971	-125.9	-4081.91	Calorimetry	20
H. Yokokawa	1989	-88.08	-4082.90	Evaluation	23
Bolech	1995	-136.1		Calorimetry	25
Jacob	1998	-133.8		EMF meas.	26
G. Rog	2002	-134.3		EMF meas.	27
A. Navrotsky	2005	About -100			
B. Wang	2008	-110.1		Evaluation	30
A. V. Radha	2009	-107.3	-4102.2	Calorimetry	29
(b) LaMnO ₃					
H.Yokokawa	1990	-48.75	-1425.1	Evaluation	4
C. Laberty	1999	-74.8	-1451.1	Calorimetry	26
K. T. Jacob	2003		-1437.99	Meas. Ev	27

2.5 Some summary and remarks

Considering on both La₂Zr₂O₇ and LaMnO₃, the Yokokawa's treatment do not need to be modified. Thus, in what follows, comparison will be made with recent experimental data by using old Yokokawa's results of a series of thermodynamic analyses.

Recently, much work has been performed on Calphad-type optimization on phase diagrams for a wide range of systems. There can be seen some belief that calorimetric values are reliable. Actually, immediately after new calorimetric values are available, the optimization has been made to take account of this new value as seen in table 1. It seems easy to do so when a limited number of elements are targeted. However, from the chemical thermodynamic point of view, the most important concern is the consistency among loosely connected thermochemical network. There can be inconsistency even among the calorimetric values. Therefore, once a set of "consistent" data was evaluated, it becomes difficult to modify those data even when new data become available.

3. Reconsideration of LSM/YSZ interface under SOFC/SOEC

3.1 Interfaces under SOFC/SOEC Operations

The interface stability of LSM/YSZ depends on equilibrium properties as well as kinetic properties. The most important variable in equilibrium properties is oxygen partial pressure or its distribution in the interface vicinity, whereas important kinetic factors are nucleation of new phases and diffusion along the chemical potential gradient in perovskite-type electrodes or the electrochemical potential gradient in electrolyte. Schematic changes in the chemical potentials in electrodes and the electrochemical potentials in electrolyte are shown in Fig. 1 for both SOFC and SOEC modes. Important points are as follows;

- (1) Overpotential of cathode in SOFC and of anode in SOEC is directly correlated with the oxygen potential difference at the three-phase-boundaries. Inside the interfaces, more drastic changes happen on the oxygen potential due to the quite low oxide ion diffusivity in LSM.

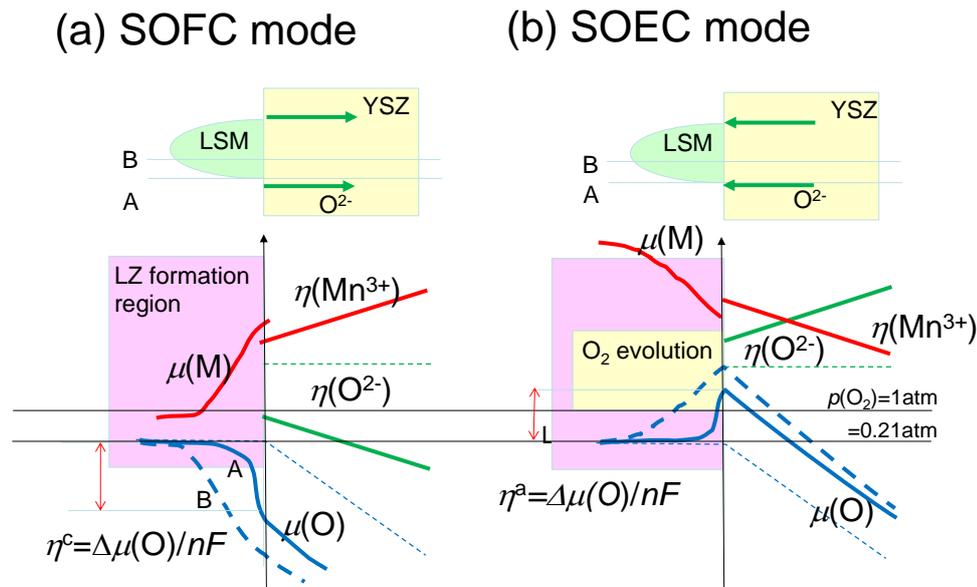


Fig. 1 Schematic changes in oxygen and metal chemical potential in electrodes and electrochemical potentials in electrolyte for SOFC and SOEC operation modes.

- (2) Under the local thermodynamic equilibrium approximation, the chemical potentials of elements exhibit inverse gradients to that of oxygen potential. Under the SOFC mode, cations are promoted to move from the interface, whereas they tend to move to the interface under the SOEC mode.
- (3) In the electrolyte, the electrochemical potential of cations provides a driving force for moving to the cathode when the cation concentration is constant. Thus, cations go to the cathode/electrolyte interface under the SOFC mode and to the inverse direction under the SOEC mode.
- (4) As illustrated in Fig. 1, the diffusion direction is the same between in electrolyte and in air electrode, but is inverse between SOFC and SOEC.

3.2 Industrial efforts in relation to LSCM/YSZ interface stability

The phase relations concerning the zirconate formation is industrially critical in optimizing the composition of LaMnO₃-based air electrode. Here, the lanthanum zirconates (LZ) formation is examined. The fundamental chemical reaction for the LZ formation can be written down as follows:



This is the oxidative reaction with partial reaction of La component in the perovskite; this leads to the separation of the stable La/Mn ratio into the La₂Zr₂O₇ formation region near to the stoichiometric region and the stable interface with A-site deficiency. In Fig. 2, the LZ formation region for non-A-site composition depends on the composition in (La,Sr,Ca)MnO₃ which is determined basically by the thermodynamic activity of LaMnO₃ component. Westinghouse established the composition of (La_{0.84}Sr_{0.16})MnO₃ although this composition is inside the LZ formation region (1). Due to the cathodic overpotential under the SOFC operation, the oxygen potential at the interface is lowered out of the LZ formation region and furthermore, driving forces for cation diffusion appear to diminish the LZ phase from the interface. Thus, the remaining phase at interfaces becomes the A-site deficient LSM; this was confirmed by also Siemens (28). On the other hand, after the

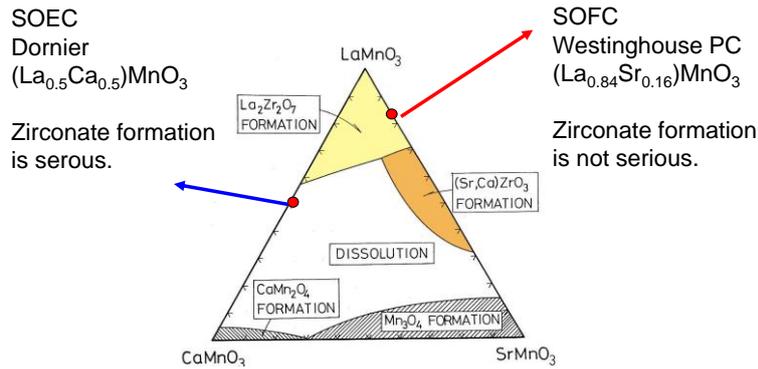


Fig. 2 zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$, SrZrO_3) formation regions for stoichiometric $(\text{La,Sr,Ca})\text{MnO}_3$ and compared with industrially optimized composition for SOFC by Westinghouse and for SOEC by Dornier (24).

optimization for the air electrode of SOEC, Dornier reached to the composition of $(\text{La}_{0.5}\text{Ca}_{0.5})\text{MnO}_3$ outside the LZ formation region. The most important issue for the air electrode of SOEC is delamination of cathode. Figure 2 suggests that the LZ formation is closely related with delamination phenomena.

3.3 the LZ formation under SOEC mode

The LZ formation becomes important with decreasing temperature or with increasing oxygen potential. This is because the existence of A-site deficiency is originated from the relatively stable Mn^{4+} ions in perovskites. Recently, many attempts have been made to clarify the LSM-YSZ interfaces under the SOEC mode (12,33-35). In particular, Keane et al. (12) observed the LZ formation under the anodic polarization not under the cathodic polarization in the symmetrical cells. Interestingly, only LZ is observed but no phases of MnO_2 or other manganese oxides are observed. Although they considered the possibility of Eq. [1], they discarded it just because the A-site deficiency is further increased. The main reason for LaMnO_3 to have the large A-site deficiency is due to the fact that the tetravalent manganese ions are well stabilized in the perovskite structure. This implies that the width of A-site deficiency should increase with decreasing temperature or with

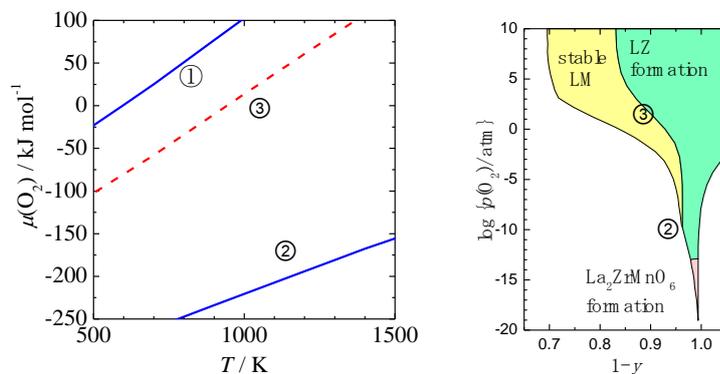
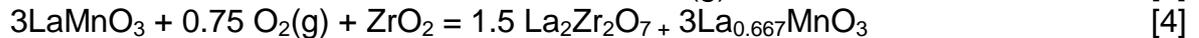


Fig. 3 Three reactions of LaMnO_3 with ZrO_2 and Effects of the La nonstoichiometry at 800 °C. Line No.1 is the oxidative decomposition given by E1.[2] in text, Line No.2 is the reductive decomposition by Eq. [3] and Line No.3 is the borderline between the LZ formation and the stable LM region given by Eq. [4] or [1].

increasing oxygen potential. The borderline of the LZ formation region and the stable LM

region was recalculated with improved data to take account of observed manganese valences (36). Calculated diagrams for the LZ formation region and the stable LM region is plotted in Fig. 3. In the left side diagram; the Gibbs energy change for the following three reactions are plotted:



The third one is based on the hypothetical constituent in the adopted ideal solution model in which $\text{La}_{0.667}\text{MnO}_3$, $\text{La}_{0.667}\text{MnO}_{2.5}$, $\text{LaMn}_{0.75}\text{O}_3$, $\text{LaMnO}_{2.5}$ are added to LaMnO_3 to take into account the nonstoichiometry of La, Mn and O.

The right-hand side diagram is calculated with MALT-CHD as the chemical potential diagram and converted to the normal concentration vs. $\log p(\text{O}_2)$ plot. The upper part of the diagram above $p(\text{O}_2)=1$ atm was newly calculated in the present investigation. Interesting points in Fig. 3 can be summarized as follows;

- (1) The calculation without consideration of the A-site deficiency predicts the oxidative decomposition at an extremely high oxygen potential. However, the calculation with nonstoichiometry predicts that no complete oxidative decomposition will not take place because of stable circumstances for the manganese tetravalent state in perovskite.
- (2) The partial oxidative LZ formation can be seen as the curved borderline between the LZ formation and the stable LM region. The straight border without change in the La/Mn ration implies that no change in valence state of manganese ions are accompanies with the LZ formation, leading to independence from the oxygen potential.
- (3) The temperature and the oxygen potential for this oxidative partial LZ formation borderline is very close to those for SOFC and SOEC modes. From this feature, it is easily concluded that the observation by Keane et al. is due mainly to the equilibrium properties caused by the relatively stable Mn^{4+} in perovskite.

Appearance of the LZ phase under the SOEC mode has not been carefully examined so far.

3.4 Sintering of LSM during fabrication or under SOFC/SOEC

Since sintering of LSM is technologically important, some features associated with sintering is discussed here.

The first example of the sintering of LSM cathode was the recognition that the A-site deficient LSM on YSZ easily loses the electrochemical activity at high temperature firing. This was the critical issue for the cathode support cells. This phenomena can be interpreted in terms of the simultaneous existence of The A-site vacancy and the oxide ion vacancy.

Recently Matsui et al. [11] and Y. L. Liu et al.[37] observed the sintering behavior of LSM cathodes under a high current density or at a large cathode overpotential. Matsui et al. adopted the slightly A-site deficient composition and Y. L. Liu et al. adopted LSM-YSZ composite cathode so that the composition of LSM must be shifted to a slightly A-site deficiency. The same criterion for LSM sintering during the fabrication can be applied to those cases. A large overpotential [38] gives rise to manganese oxide precipitation on YSZ to form the Mn bands. This is partly because the A-site deficient LSM becomes unstable against the Mn oxide precipitation.

Sintering of LSM under the SOEC mode was recently observed by Yoon et al. (35) who interpreted it in terms of the increasing number of created cation vacancies under a large anodic polarization. This is apparently different mechanism from those described above. As illustrated in Fig. 1, the large oxygen potential difference will appear at the anode-electrolyte interface under the SOEC mode. At the high oxygen potential region, oxygen incorporate and the cation vacancies are created, leading to high diffusivity. This suggests

that in the vicinity of the LSM-YSZ interface, LSM sintering may be enhanced. This can explain why sometimes the delamination takes place inside LSM electrode slightly apart from the interface.

Inside the electrolyte, driving forces for cations to move from the interface to inside occur under the SOEC mode. Since the diffusion of Mn in YSZ is rather high, it is reasonable to form pores inside the YSZ near to the interface. When the LZ formation may occur at the interface, this may block further flow of Mn from the electrode to the electrolyte. This view is consistent with the observation.

The present considerations have revealed the importance of the LZ formation, Mn diffusion in YSZ and also cation diffusion in LSM. Under a large cathodic polarization, there is a possibility of Mn oxide precipitation. Even for the LZ formation or Mn oxide precipitation, diffusion processes are involved. Thus, the stability of LSM-YSZ interface under the SOFC/SOEC mode is governed by many kinetic properties. In view of this, a new attempt of Hughes et al.(34) seems to be quite interesting to identify what kinds of factors becomes important under a given relaxation time or under a given current density (overpotential, in other words, oxygen potential).

4. Summaries

The present investigation places an importance on the equilibrium properties which LSM-YSZ interfaces are concerned. Some experimental results can be well interpreted in terms of such equilibrium properties alone. Even so, there are many kinetic factors controlling the stability of LSM-YSZ interfaces.

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