Calculations of Thermodynamic Properties for Undoped and Sr- Doped $LaMnO_3$ Perovskite Oxides①

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Abstract The thermodynamic data of undoped and Sr- doped $LaMnO_3$ perovskite oxides have been calculated, which is in fair agreement with the experimental results. These thermodynamic data may be used to estimate the chemical stability of the compounds and also their reactivity with other materials.

Key words: thermodynamic data; $LaMnO_3$; $La_{1-x}Sr_xMnO_3$

中图分类号: TB34 文献标识码: A 文章编号: 1007- 855X(2002)01- 022- 03

The $La_{1-x}Sr_xMnO_3$ (LSM) is the current cathode materials used in Solid Oxide Fuel Cell (SOFC) due to its high electrical conductivity, good electrocatalytic activity for the reduction of oxygen, and good thermal expansion matches to the other components.[1, 2]

At present many studies on the electrical or catalytic properties and preparation methods of LSM have been reported. Since the materials are often used at high temperature and sometimes in highly oxidizing atmosphere, thermodynamic function values are needed to estimate the chemical stability of the compounds and also their reactivity with other materials. However, there are few reports on the thermodynamic properties. Kuo et al.[3] found that the relative partial molar enthalpy is about -115 ± 13 kJ/mol and independent of Sr content in LSM. Hildrum et al.[4] measured the standard free energy of decomposition reaction for $La_{0.8}Sr_{0.2}MnO_3$ (LSM- 20) by use of the solid electrolyte galvanic cell method. Feng Zheng et al.[5] reported SrO activity in LSM decreased with increasing temperature and increasing Sr content on the base of experimental study. Apparently, these limited experimental data are not sufficient to provide a full understanding of the materials behaviors for the cathodes in SOFC application.

The purpose of the present study was to calculate the thermodynamic data of the undoped and Sr- doped $LaMnO_3$ perovskite.

1 $LaMnO_3$ perovskite

$LaMnO_3$ is a - type perovskite oxide, which is orthorhombic at room temperature and shows an orthorhombic- rhombohedral crystall- ographic transition at about 670 K[1]. Using the basic data of $LaMnO_3$[6,7], we calculated the heat capacity (C), standard enthalpy ($H^{\ddot{i}}$), entropy ($S^{\ddot{i}}$) and free energy ($G^{\ddot{i}}$) at different temperature, as shown in Table 1. Moreover, the variation in standard free energy ($\Delta G^{\ddot{i}}$) of the reaction as follow is calculated, listed in Table 2.

$$LaMnO_3 = 1/2La_2O_3 + MnO + 1/4O_2 \quad (1)$$

① 收稿日期: 2000- 10- 19;
基金项目: 云南省选冶新技术重点实验室资助项目;
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Table 1　Thermodynamic data of $LaMnO_3$

T/K	C / J(mol·K)$^{-1}$	$H^{\ddagger}$/ kJ·mol^{-1}	$S^{\ddagger}$/ J(mol·K)$^{-1}$	$G^{\ddagger}$/ kJ·mol^{-1}
298	103.90	−1 425.10	130.50	−1 463.99
400	113.76	−1 413.94	162.60	−1 478.98
600	122.72	−1 390.18	210.64	−1 516.57
675	124.91	−1 380.89	225.50	−1 533.10
		4.0	5.92	
675	124.91	−1 376.89	231.42	−1 533.10
800	128.00	−1 361.08	252.63	−1 563.18
1 000	132.22	−1 335.05	281.66	−1 616.71
1 200	136.02	−1 308.22	306.11	−1 675.55
1 400	139.62	−1 280.65	327.35	−1 738.94
1 600	143.11	−1 252.38	346.22	−1 806.33
1 800	146.55	−1 223.41	363.27	−1 877.30
2 000	149.94	−1 193.76	378.89	−1 951.54
2 200	153.31	−1 163.44	393.34	−2 028.79
2 400	156.67	−1 132.44	406.82	−2 108.81
2 500	158.34	−1 116.69	413.25	−2 149.82

Table 2　The standard free energy ($G^{\ddagger}$) of LSM−20 and variation in standard free energy ($\Delta G^{\ddagger}$) of decomposition reaction for $LaMnO_3$

T/K	$G^{\ddagger}$/ kJ·mol^{-1}	$\Delta G^{\ddagger}$/ kJ·mol^{-1}
298	−1 400.73	130.22
300	−1 401.01	130.13
400	−1 415.81	125.66
500	−1 434.69	121.19
600	−1 453.58	116.70
700	−1 476.53	112.65
800	−1 499.48	108.60
900	−1 525.59	104.86
1 000	−1 551.67	101.11
1 100	−1 580.35	97.43
1 200	−1 609.02	93.75

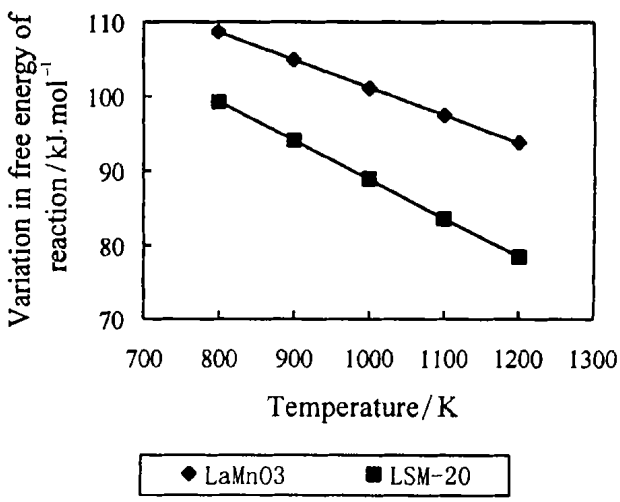

Fig. 1　Variation in free energy of decomposition reaction for $LaMnO_3$ and LSM

2　LSM perovskite

Hildrum et al. [4] studied the relationship between temperature and the variation in the standard free energy of decomposition reaction as follow:

$$La_{0.8}Sr_{0.2}MnO_3 = 0.4La_2O_3 + MnO + 0.2SrO + 0.3O_2 \quad (2)$$

Thus we calculated the standard free energy for LSM−20 and listed in Table 2.

3　Discussion

The standard formation free energy of $LaMnO_3$ calculated using the data in the table 1 and the relative data [8] coincides with the result in reference [6], as shown in Table 3.

A comparison between the variation in standard free energy of decomposition reaction for $LaMnO_3$ and $La_{0.8}Sr_{0.2}MnO_3$ (LSM−20) with temperature is presented in Fig. 1. And the calculated results of decomposition reaction for $LaMnO_3$ based up on the Fig. 1 are in fair agreement with the experimental results measured via TG and the electric−conductivity method, as shown in Table 3.

The decomposition temperature calculated for $LaMnO_3$ and LSM – 20 are about 3 301 K and 2 709 K, respectively, which implied that LSM cathodes are stable when SOFC systems operate at 1 000℃. At high temperature, the materials can have oxygen excess, stoichiometry, or deficiency depending on oxygen partial pressure, and the critical oxygen partial pressure depends on temperature, shifting to higher values at higher temperature for $LaMnO_3$ oxide[1]. Although strontium doping enhances the electronic conductivity of $LaMnO_3$ by increasing the Mn^{4+} content by the substitution of La^{3+} by Sr^{2+}

Table 3 Comparison between calculated and experimental results for $LaMnO_3$ formation and decomposition reaction

Denotation	T / K	Calculated result/ kJ·mol^{-1}	Experimental result/ kJ·mol^{-1}	Reference
$\Delta_f G^{\ddot{i}}$	298	– 1 345.79	– 1 345.8	[6]
$\Delta G^{\ddot{i}}$	1 273	90.75	89.02	[4]
$\Delta G^{\ddot{i}}$	1 373	87.03	85.70	[4]

$$LaMnO_3 \xrightarrow{SrO} La_{1-x}^{3+}Sr_x^{2+}Mn_{1-x}^{3+}Mn_x^{4+}O_3 \quad (3)$$

Anomalous scatter that was observed for $La_{0.8}Ca_{0.2}CrO_3$ oxide by Natsuko Sakai et al.[9] also may be occurred in the heat capacity determinations for LSM oxides probably due to reduction of tetravalent manganese– ions. Such a reduction is accompanied by liberation of oxygen as expressed in the following reaction:

$$La_{1-x}^{3+}Sr_x^{2+}Mn_{1-x}^{3+}Mn_x^{4+}O_3(s) \longleftrightarrow La_{1-x}^{3+}Sr_x^{2+}Mn_{1-x+2\delta}^{3+}Mn_{x-2\delta}^{4+}O_{3-\delta} + \delta/2O_2 \quad (4)$$

Using Kröger– Vink notation the above reaction can be formulated as follows:

$$2Mn_{Mn} + O_O^{\times} \longleftrightarrow Mn_{Mn}^{\times} + V_{\ddot{o}} + 1/2O_2(g) \quad (5)$$

Where Mn_{Mn} is Mn(Ⅳ) – ion at a Mn(Ⅲ) lattice position, $O_O^{\times}$ and $Mn_{Mn}^{\times}$ are an oxide ion and a Mn(Ⅲ) – ion in the perovskite lattice respectively, and V_o is an onygen vacany.

Therefore, the thermodynamic properties for LSM perovskite oxides must be studied in detail because the oxygen vacancy formation for the oxides becomes significant at high temperature or reducing atmosphere.

4 Conclusions

The thermodynamic data of $LaMnO_3$ and LSM – 20 were calculated, which is in fair agreement with the experimental results, and indicates LSM cathodes are stable at oxidizing atmosphere when SOFC systems operate at 1 000℃. But the thermodynamic properties for LSM oxides must be studied in detail for $LaMnO_3$ and LSM oxides exhibits excess, stoichiometry, or deficiency in different oxygen content, which may be resulted in the anomalous phenomena occurring.

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未掺杂与 Sr 掺杂的 $LaMnO_3$ 钙钛矿氧化物热力学计算

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摘要: 计算了未掺杂与 Sr 掺杂的 $LaMnO_3$ 钙钛矿氧化物的热力学数据. 计算与实验结果吻合较好. 这些热力学数据可以用来估计复合物的化学稳定性值以及与其它材料间的化学反应性.

关键词: 热力学数据; $LaMnO_3$; $La_{1-x}Sr_xMnO_3$