THERMODYNAMIC STUDIES OF SOME COMPOSITE CATHODES USED IN SOFC

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ABSTRACT

When searching improved cathode materials for use in solid oxide fuel cells (SOFC), a thorough knowledge of the thermodynamics of the new materials is very important. The solid-oxide electrolyte galvanic cell method was selected to study the thermodynamic properties of some composite materials based on lanthanum strontium ferrite manganite, so that the better accuracy of this technique could be fruitfully exploited. The relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium oxygen pressures are obtained in the temperature range of 1073-1273 K. By solid state coulometric titration, the initial composition of the perovskite phases was altered under controlled conditions. The variation of the thermodynamic properties with the oxygen relative stoichiometry change is discussed. The results evidence the influence of the iron content on the thermodynamic properties.

INTRODUCTION

Among the conducting transition metal oxides with perovskite structure, the composite materials based on lanthanum strontium ferrite manganite are becoming very important because of promising application as cathodes for solid oxide fuel cells.

Alongside the determination of their electrical and structural characteristics, a
thorough knowledge of the chemistry and thermodynamics of the new materials is very important. Although in the perovskite type oxides La$_{1-x}$Sr$_x$MnO$_{3+x}$ theoretical [1-3] and experimental [4-6] studies regarding the phase stability and the thermodynamic properties have been reported, in the case of multicomponent oxides of general formula La$_{1-x}$Sr$_x$Mn$_{1-y}$Fe$_y$O$_3$, the thermodynamic data are not available.

As we revealed in a previous paper [6], the thermodynamic stability limits of nonstoichiometric lanthanum manganites and lanthanum strontium manganites are conveniently situated within the range of oxygen chemical potentials which can be measured by galvanic cells incorporating ZrO$_2$(Y$_2$O$_3$) solid electrolyte and an iron-wüstite reference electrode.

In the present study, new measurements have been made by EMF solid electrolyte galvanic cells method in order to characterize from the thermodynamic point of view the following perovskite-type materials:

La$_{0.7}$Sr$_{0.3}$Mn$_{0.8}$Fe$_{0.2}$O$_3$, La$_{0.7}$Sr$_{0.3}$Mn$_{0.3}$Fe$_{0.7}$O$_3$, and La$_{0.7}$Sr$_{0.3}$Mn$_{0.5}$Fe$_{0.5}$O$_3$.

The measurements are effected within the 1073-1273 K temperature range and the partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium partial pressures of oxygen are obtained as a function of temperature. The influence of the oxygen stoichiometry change on the thermodynamic properties is discussed using the data obtained by a coulometric titration technique coupled with EMF measurements. The results evidence the effect of the iron content on the thermodynamic properties.

**EXPERIMENTAL**

The experimental method and apparatus are previously described [6]. Their principal characteristics are:

- The geometry of the work cell ensures a compact electrode electrolyte assembly, so that temperature uniformity is easily reached and the extraneous thermoelectric potentials are minimized.

- The measurements are effected in vacuum at a residual gas pressure of $10^{-4}$-$10^{-5}$ Pa, after a previous rinsing of the installation with purified argon. The enclosure and the isolation of the electrodes provides an adequate solution to remove the oxygen transfer between the electrodes through the gas.

- Prevention of signal pick-up from external heating sources is achieved by the use of a non-inductive furnace and the earthed screening of cell and leads.

**Materials**

The solid electrolyte is a disc of 12.84 wt% yttria stabilized zirconia (10 mm
diameter, 6 mm thick) supplied by Risø National Laboratory, Roskilde, Denmark.

The powder of the specimens were supplied by Haldor Topsøe A/S, Lyngby, Denmark. These were prepared by drip pyrolysis and were characterized by X-ray powder diffraction as single perovskite phases [7, 8]. The powders were pressed into small pellets (2 mm thick and 2 mm high) weighing 70 mg and were sintered at 1273 K in air for four hours.

The reference electrode and also, the counter electrode in the case of coulometric titration measurements are both prepared from electrolytic iron and Fe2O3 powders mixed in a molar ratio of 4 : 1, pressed at 15MPa and sintered at 1373 K in vacuum for 12 hours.

Measurements

After the cell was rinsed with pure argon, the installation was emptied to ~10^-4 Pa and slowly heated. The heating is gradually performed at a constant rate, so that the rest of the pressure in the apparatus would not surpass 10^-3 - 10^-4 Pa. The temperature gradient across the cell must be less than 1 K.

The EMF measurements are undertaken with a Keithley 197 microvoltmeter. The electromotive force is measured at increasing and decreasing temperature, within the 1073 - 1273 K range. The readings are made at 50 K intervals, every time waiting till the equilibrium values are recorded. The determinations were considered as being satisfactory when values for increasing and decreasing temperature agreed within 1 or 2 mV.

After the measurements were completed over a range of temperatures, at a constant composition, oxygen was removed from the sample by solid state coulometric titration [9, 10] using a Bi-PAD Tacussel Potentiostat. Both titration and equilibration were carried out at 1173 K in vacuum at a pressure of 10^-4 Pa.

According to Faraday's law, the mass change |Δm| (g) of the sample is related to the transferred charge Q (A·sec) by:

\[ |Δm| = 8.291 \times 10^{-4} Q \]  

[1]

The quantity of electricity passed through the cell was the same for all the samples and corresponded to a relative change in nonstoichiometry of Δδ = 0.004. After the desired amount of electricity was passed through the cell, the current circuit was opened and sufficient time (about three hours) was allowed for the electrode to equilibrate. Then, by changing the temperature under the open-circuit condition, the change of EMF with temperature was again determined at this new composition of the
From the steady state EMF, the partial molar quantities and the equilibrium pressures of oxygen were calculated. The results have been analysed in order to evidence the variation of the thermodynamic properties with the relative nonstoichiometry change $\Delta \delta$.

RESULTS AND DISCUSSION

The chemical potential of oxygen in the perovskite-type oxides was measured by using galvanic cells of the type:

$$(-) \text{Fe, wüstite} / \text{ZnO}_2(Y_2O_3) / \text{ABO}_3 (+)$$

[1]

were, for simplicity, we noted with $\text{ABO}_3$ a (La,Sr)(Mn,Fe)O$_3$ perovskite-type oxide. Since the electrolyte of the cell shows only ionic conduction due to migration of oxygen ions in the electrolyte, the virtual cell reaction may be expressed in terms of oxygen transfer from the right-hand to the left-hand electrode. Hence the EMF of the cell is:

$$E = \frac{\mu_{O_2} - \mu_{O_2(\text{ref})}}{4F}$$  \[2\]

where $\mu_{O_2}$ and $\mu_{O_2(\text{ref})}$ are, respectively, the oxygen chemical potentials of the perovskite and of the reference electrode, and $F$ is the Faraday constant. Upon substituting the experimental values of $E$ in the above equation and knowing the free energy change of the reference electrode reaction evaluated from calorimetrically verified gas equilibrium measurements [11,12]:

$$\Delta G_{\text{Fe, wüstite}}^0 (\pm 0.523) = [-264.575 + 0.065 T] \text{kJ mol}^{-1}$$  \[3\]

the values of the relative partial molar free energy of the solution of oxygen in the perovskite phase and hence the pressures of oxygen in equilibrium with the solid can be calculated.

$$\Delta \tilde{G}_{O_2} = RT \ln p_{O_2}$$  \[4\]

The relative partial molar enthalpies and entropies were obtained according to the known relationships:

$$\frac{\delta \Delta \tilde{G}_{O_2}}{\delta T} = -\frac{\Delta \tilde{H}_{O_2}}{T^2}$$  \[5\]

$$\Delta \tilde{G}_{O_2} = \Delta \tilde{H}_{O_2} - T \Delta \tilde{S}_{O_2}$$  \[6\]

The variation of the thermodynamic data with the change in the oxygen...
stoichiometry in the selected group of lanthanum strontium ferrite manganites, at the same strontium content (30%), can be discussed only being related to the effect of the iron content.

The representative results obtained before and after titration are depicted in figures 1-7 were the data are plotted for the three compounds: $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.3}\text{Fe}_{0.7}\text{O}_3$ (noted as S1, S2 and S3, respectively) which differ between them only by the iron content.

The partial molar free energy is a linear function of temperature. The partial molar enthalpies and entropies are consequently independent of temperature.

As one can see in figure 2, the $\Delta G_{\text{O}_2}$ values obtained before titration for the sample with 70% iron is $\sim 28 \text{ kJ mol}^{-1}$ (at 1073 K) and $\sim 37 \text{ kJ mol}^{-1}$ (at 1273 K) more negative compared with the values found for the sample with 20% iron. The values of $\Delta H_{\text{O}_2}$ and $\Delta S_{\text{O}_2}$ (figure 7) increase correspondingly at a higher iron content with $\sim 20 \text{ kJ mol}^{-1}$ and $\sim 45 \text{ J mol}^{-1}$, respectively. The increasing of the partial molar heats of solution with the increasing of iron content, suggests the change of the mechanism of conduction in the compounds with high iron content.

In figures 3 - 7, two sets of data obtained before and after the isothermal titration experiments are plotted.

It will be seen that, after titration (figure 3), although the variations with temperature of the partial molar energies have the same general trend, the effect of the iron content is more little evident at smaller temperatures. Instead, at 1273 K, a difference of $\sim 17 \text{ kJ mol}^{-1}$ is obtained between the $\Delta G_{\text{O}_2}$ values of the samples with 70% and 20% iron, respectively.

Comparing the changes of $\Delta G_{\text{O}_2}$ and log $p_{\text{O}_2}$ values with temperature at the same composition, before and after titration experiments (figures 4 and 6), one can observe that the oxygen stoichiometry change has an opposite effect depending of the iron content. Thus, the $\Delta G_{\text{O}_2}$ and log $p_{\text{O}_2}$ values decrease after titration for the sample with 20% iron and increase for the sample with 70% iron. Regarding the changes of $\Delta H_{\text{O}_2}$ and $\Delta S_{\text{O}_2}$ (figure 7), one can observe that for compositions with small and medium iron content, both the variations of enthalpy and entropy decrease with the stoichiometry change. Instead, for the composition with high iron content, higher values of $\Delta H_{\text{O}_2}$ and $\Delta S_{\text{O}_2}$ are obtained after titration. This statement suggests that in the case of composition with high iron content, the predominant defects are different comparatively with those of the samples with small and medium iron content and the oxygen vacancies distribute randomly on the oxygen sublattice of the perovskite-type structure.
CONCLUSIONS

The subject of the present paper is intended as an attempt to broaden the potentialities of solid state EMF techniques in thermodynamic studies of the perovskite-type composite materials. The obtained results are considered as preliminary data of a set of experiments in the study of some selected lanthanum strontium ferrite manganites.

In the case of compounds studied in this paper the variation of thermodynamic properties with the oxygen relative stoichiometry change can be discussed only being related to the effect of the iron content.

In the future, systematic studies in a larger region of oxygen nonstoichiometry will give further details on the defect equilibrium and on the variation of the thermodynamic properties with the oxygen nonstoichiometry in lanthanum strontium ferrite manganites.

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Fig. 5. The plot of \( \log p_{O_2} \) vs. \( 1/T \) before and after titration (the samples S1 and S3).

Fig. 6. The plot of \( \log p_{O_2} \) vs. \( 1/T \) before and after titration (the sample S2).

Fig. 7. \( \Delta H_{O_2} \) and \( \Delta S_{O_2} \) as a function of iron content before and after titration.