Thermoelectric power of Gd-doped CeO$_2$ (Gd$_{0.1}$Ce$_{0.9}$O$_{(2-\delta)}$ (GDC10)): Measurements on porous samples

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Abstract

Thermoelectric power was measured on dense and porous samples of two materials: silver, a noble metal, and Gd-doped CeO$_2$ of composition Gd$_{0.1}$Ce$_{0.9}$O$_{(2-\delta)}$ (GDC10), a mixed ionic electronic conductor. Since silver does not change composition when subjected to a change in temperature, only thermal equilibration is required. Both dense and porous samples of silver equilibrated in about the same time, and the measured thermoelectric power was also about the same. However, the time required for equilibration in dense GDC10 samples was an order of magnitude greater as compared to that for porous samples. The measured thermoelectric power on dense samples was also different from that on porous samples, especially below 600 °C. It was also observed that the measured thermoelectric power in dense GDC10 samples depended on thermal history unlike porous GDC10 samples. That is, prior thermal annealing history affected subsequent measurements at lower temperatures in the case of dense samples. Issues relating to the kinetics of EMF equilibration in dense and porous samples of silver and GDC10 are discussed.
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1. Introduction

Measurements of thermoelectric power or Seebeck coefficient on many metallic elemental materials and alloys have been reported for over 50 years [1–7]. The typical procedure consists of heating a bar-shaped sample to desired temperature, T, imposing a small temperature difference, ΔT, across the sample, and measuring the corresponding voltage or EMF difference developed, $\Delta\phi$. Then, the ratio

$$-\left(\frac{\Delta\phi}{\Delta T}\right)_{\Delta T \to 0} \tag{1}$$

is defined as the thermoelectric power (Seebeck coefficient) of the material/system, which includes homogeneous and heterogeneous contributions (e.g., reactions at the contacts), and the connecting wire contribution. Measurements on metals are made either in air if the sample does not oxidize, or in an inert atmosphere or in vacuum if it is not oxidation resistant. Electrons are the electrically charged mobile species, which transport under imposed temperature gradient. With the exception of point defect

concentrations, no other changes are expected upon change of temperature, assuming there are no phase or compositional changes.

Measurement and analysis of thermoelectric power of inorganic materials has also been the subject of much interest over the past few decades [1,8–31]. Measurements on halides were typically done in air. Most halides exhibit very small non-stoichiometry and negligible composition changes occur when heated in air. However, many oxides exhibit significant stoichiometry ranges and undergo compositional changes when heated in air. A typical oxide may be represented as MO$_{y\pm\delta}$ where the non-stoichiometry, δ, depends upon temperature, T, and oxygen partial pressure, p_{O_2}, i.e., $\delta = \delta(T, p_{O_2})$. When heated at a fixed p_{O_2}, e.g., in air, changes in stoichiometry generally occur. Small changes in δ often lead to large changes in defect concentrations, and this also can lead to significant changes in those properties that depend upon defect concentrations.

Changes in composition require incorporation or removal of oxygen by chemical diffusion.[1] If the chemical diffusion coef-

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[1] Actually, another parameter involving transfer across gas-solid interface, k_{chem}, with units of cm s^{-1} can also affect the overall kinetics of oxygen incor-

ficient of oxygen in the material is $\tilde{D}_O$ and if the sample is a plate of thickness $2d$ (smallest dimension), approximate time necessary for sample equilibration with the imposed atmosphere is $\sim d^2/\tilde{D}_O$. An unequivocal determination of any physical or chemical property, which depends upon defect types and concentrations is possible only if the sample has equilibrated under the imposed experimental conditions. In addition, the kinetic parameter that determines the kinetics of equilibration, namely $\tilde{D}_O$, also depends on types, concentrations and mobilities of defects. The $\tilde{D}_O$ can vary over a wide range depending upon material, composition, the imposed atmosphere, and temperature. Suppose $2d$ is 2 mm and $\tilde{D}_O$ is 10^{-7} cm^2 s^{-1} under the imposed conditions. Then, the approximate equilibration time, $d^2/\tilde{D}_O$, is 10^5 s or $\sim$27 h. Most solids exhibit much lower $\tilde{D}_O$ (again, depending upon composition, atmosphere and temperature), and sample equilibration may not occur during a typical experiment. Thus, accurate measurement of thermoelectric power, corresponding to equilibrium conditions, may be difficult using dense samples, especially at low temperatures. Three types of response are expected using thick, dense samples during thermoelectric power measurements. (a) If $\tilde{D}_O$ is sufficiently high, the voltage may reach a stable value rapidly, and the measured thermoelectric power will correspond to sample having equilibrated under experimental conditions—the objective of the experiment. (b) If $\tilde{D}_O$ is very small, the composition would have hardly changed during the measurement. In such a case, the EMF will once again equilibrate rapidly. However, the measured thermoelectric power will correspond to non-equilibrium conditions, insofar as the composition of the sample is concerned. Mobile defects will transport and equilibrate to imposed temperature differential. However, defect concentrations will still correspond to non-equilibrium conditions under imposed temperature and atmosphere. Thus, even if EMF equilibrates rapidly, the measured thermoelectric power will not correspond to equilibrium conditions. This aspect can be conveniently studied by annealing identical samples at different (and high) temperatures followed by measurement of thermoelectric power at a much lower temperature. The measured thermoelectric power on samples annealed at different temperatures will be different even if the measurement temperature is identical. (c) If $\tilde{D}_O$ is intermediate to the above two cases, the EMF may not readily stabilize during a typical experiment, and in such a case, it will not be possible to measure thermoelectric power in a reasonable period of time. In such cases, long equilibration times may be required.

In metals, the time required for equilibration of EMF is the same as the time required for thermal equilibration, given by t_{eq}^T. This corresponds to the time required for the ends of the sample to achieve stable temperatures, which depends on system thermal inertia (including gas phase) described by a heat transfer coefficient, h, thermal diffusivity, α, and sample geometry and dimensions. For most experimental set ups, t_{eq}^T, is about few minutes.

In the case of an oxide, $MO_{y \pm \delta}$, with $\delta = \delta(T, p_{O_2})$, both composition and temperature equilibration must occur. If composition equilibration is faster than thermal equilibration, that is if $t_{eq}^C \approx d^2/\tilde{D}_O << t_{eq}^T$, where t_{eq}^C is the time required for compositional equilibration, the EMF equilibration will require time $\sim t_{eq}^T$. However, if $d^2/\tilde{D}_O >> t_{eq}^T$, then EMF equilibration will require time $\sim t_{eq}^C \approx d^2/\tilde{D}_O$. In such a case, the measured thermoelectric power may correspond to non-equilibrium conditions (assuming experiment is conducted for time $<< d^2/\tilde{D}_O$), and not representative of thermodynamic equilibrium—and thus not a unique material parameter. For a sample thickness of 2 mm and with $\tilde{D}_O \sim 10^{-7}$ cm^2/s or smaller, equilibration time is several hours or days or longer. Thus, to facilitate the measurement of thermoelectric power corresponding to true equilibrium conditions in a typical experiment, $d^2/\tilde{D}_O$ should be on the order of minutes or at the most a few hours. This is difficult to achieve in many oxides when using dense samples due to sluggish oxygen diffusion.

Now suppose a porous sample of contiguous porosity, with particle radius, r, on the order of microns, and sample thickness $\sim$2 mm is used. Gas diffusivity through porous bodies is generally $\sim$0.1 to 1 cm^2 s^{-1}, depending upon gas type, sample porosity, and tortuosity factor. Even if one assumes the lower value, gas phase equilibration within pores occurs rapidly, in about $(0.1$ cm$)^2/0.1$ or in 0.1 s. Subsequent solid state diffusion of oxygen requires time $\sim r^2/\tilde{D}_O$. For r of 1 μm, equilibration time, $r^2/\tilde{D}_O$, is $\sim$0.1 s for $\tilde{D}_O \sim 10^{-7}$ cm^2 s^{-1}, instead of $\sim$27 h for a dense sample of 2 mm thickness! If $\tilde{D}_O \sim 10^{-10}$ cm^2 s^{-1}, equilibration time for the porous sample is $\sim$100 s versus $\sim$27,000 h for the dense sample. This shows that a porous body should equilibrate with the atmosphere in a reasonable time unlike a dense body, and the use of a porous sample should facilitate the measurement of thermoelectric power corresponding to equilibrium conditions.

The preceding discussion shows that whether the sample used is porous or dense should also affect the measured stoichiometry during a typical cooling step from a high temperature. In an oxide $MO_{y-\delta}$, where δ increases with increase in temperature, the measured δ for porous and dense bodies during cool down will vary with temperature schematically as shown in Fig. 1. Thus, the use of a porous sample instead of a dense sample should facilitate the measurement of thermoelectric power corresponding to equilibrium conditions. Fig. 2(a) shows a schematic of the kinetics of composition equilibration in a dense body where gradation in color (dark grey to light grey) indicates diffusion profile. Fig. 2(b), on the other hand, shows a porous body of about the same external dimensions as the dense body. However, the composition equilibration occurs rapidly—this is indicated by a uniform color (uniform grey) within each particle.

The approach of using porous samples for the measurement of thermoelectric power has been recently demonstrated by the authors on proton conducting $Ba_3Ca_{1.18}Nb_{1.82}O_{(9-\delta)}$ (BCN18) [32]. This work showed that stable values of EMF could be obtained on porous samples, but not on dense samples, especially below $\sim$600 °C. Above 700 °C, it was shown that the thermoelectric power measured on dense and porous samples was about the same. However, the time required for equilibra-
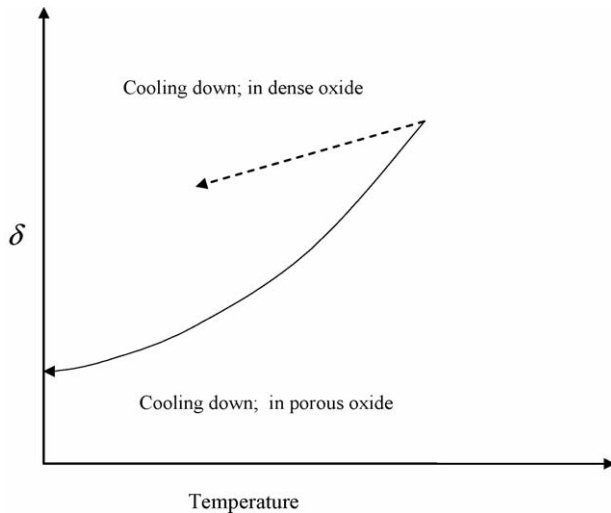
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poration/expulsion. In the present discussion, this aspect is ignored, but can be readily included.

Fig. 1. Schematic variation of δ in $MO_{y-\delta}$ during cool down in dense and porous samples. It is assumed that at high temperatures, both dense and porous samples are equilibrated so that δ is the same in both samples. During cool down, the porous sample is much more likely to equilibrate with the atmosphere due to fast kinetics, but not the dense one. Thus, in a typical experiment wherein the samples are cooled over a few hours, δ in porous samples will be close to the equilibrium state, but δ in dense samples will not be unique, and will depend upon the cooling history (rate).

tion was much longer when using dense samples. The present manuscript describes work on rare earth oxide doped cerium oxide, using both dense and porous samples. Samples of nominal composition $Gd_{0.1}Ce_{0.9}O_{(2-\delta)}$ (GDC10) were fabricated. Experiments were conducted on dense and porous samples. Experiments were also conducted on dense and porous samples of silver. Experiments on GDC10 were conducted in air over a temperature range from 400 to 800 °C. Experiments on silver were conducted in vacuum at 100 °C.

2. Experimental procedure

2.1. Fabrication of silver samples

Dense, bar-shaped samples of silver were fabricated by die-pressing silver powder (Alfa Aesar) and annealing at 400 °C for 1 h. For the fabrication of porous samples, silver powder was lightly die-pressed and annealed at 400 °C for 1 h. The density of porous silver samples was measured by the Archimedes method, and the resulting density was ∼85% of theoretical (15% porosity). Although this porosity was not quite satisfactory, the contamination problem that had occurred in the earlier work was eliminated [32].

2.2. Fabrication of GDC10 samples

The samples of $Gd_{0.1}Ce_{0.9}O_{(2-\delta)}$ were prepared using commercial powder (Praxair), which was die-pressed, isostatically pressed under a pressure of ∼2000 kg cm^{-2}, and sintered in air at 1400 °C for 2 h. Samples with a density above ∼99% of theoretical (7.216 g ml^{-1}), as measured by the Archimedes method, were obtained [14]. Dense samples had a thickness of ∼1 mm. For the fabrication of porous samples, carbon powder (HTW,
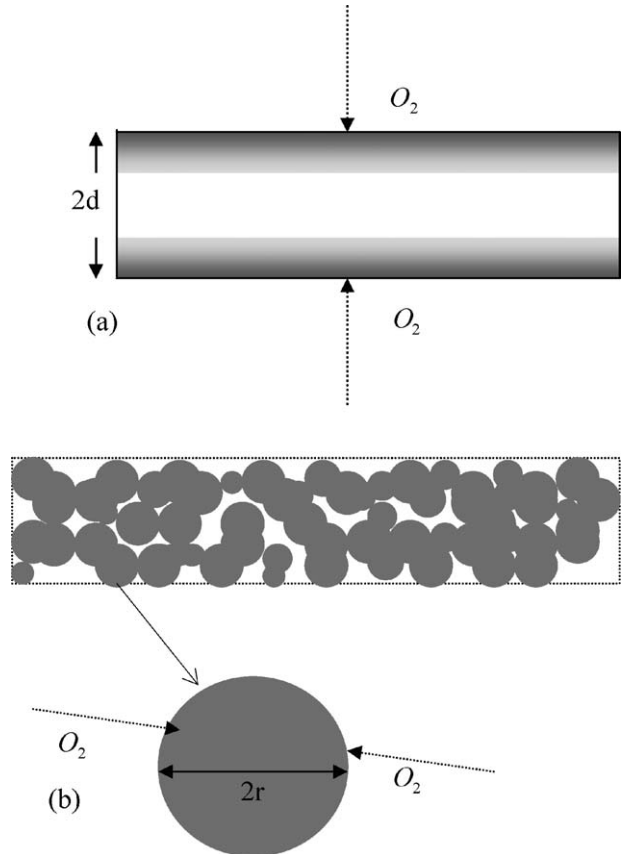

Fig. 2. (a) A schematic representation showing the change in composition occurring in a dense body under imposed conditions as the sample attempts to equilibrate. Because of sluggish diffusion through a dense body of a relatively large thickness, $2d$ (in the millimeter range), the composition does not equilibrate during the course of a typical experiment. This is shown by the gradation in color. (b) A schematic representation showing the change in composition occurring in a porous body when exposed to a different atmosphere. Because of the short diffusion distance, composition within individual particles of a porous body equilibrates relatively quickly. This is shown by a uniform color within individual particles.

10–20 μm) was mixed with the GDC10 powder in ethanol for 24 h. After drying, bar-shaped samples were die-pressed, isostatically pressed, and sintered in air at 1400 °C for 2 h. The resulting density of porous samples was ∼76% of theoretical (∼24% porosity, most of which was open porosity).

2.3. Measurement of thermoelectric power

The testing set-up used consists of a horizontal tube furnace, into which a quartz tube was inserted (Fig. 3). Platinum paste was
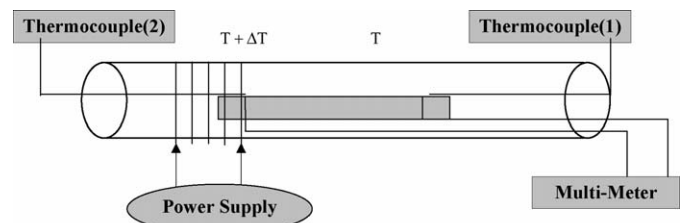

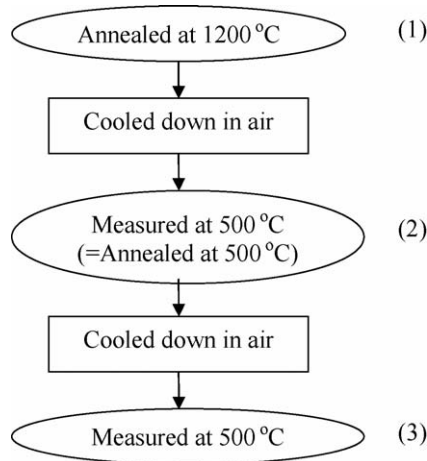Fig. 3. Experimental set-up used in the present work.

Fig. 4. Experimental procedure used for heat treatments on dense and porous GDC10 and the measurement of thermoelectric power (effect of thermal history).

applied to the ends of a bar-shaped sample, to which platinum wires were attached. A platinum wire heater was wound on a segment of the quartz tube. One end of the sample was positioned at the center of the platinum heater, connected to a power supply. Measuring tips of two s-type thermocouples (Pt/Pt–10%Rh) were attached to the platinum electrodes on the GDC10 sample. Thermoelectric power measurements were conducted on dense and porous samples of GDC10 in the temperature range from 400 to 800 °C. The desired atmosphere (ambient air at $p_{O_2} \sim 0.21$ atm) was circulated through the quartz tube. Furnace temperature was varied between ~500 and ~800 °C. Power to the platinum heater was separately supplied.

In the case of silver samples, s-type thermocouples were positioned on both ends of the face of the sample, but no currents were detected between the silver sample and the Pt/Pt–10%Rh thermocouples. The thermoelectric power of silver was measured under vacuum to avoid parasitic thermal conduction [2]. Because the vacuum equipment in this experimental set-up could not be used at high temperatures, the measurements were conducted at 100 °C.

The temperature difference between the two ends of the sample, ΔT, was measured via the two thermocouples. The EMF generated across the two ends of the sample, $\Delta \phi$, was measured using a Keitheley 2000 multi-meter. Lab View^{TM} software was used to record the data. The ratio as defined in Eq. (1) was determined, and is reported here as the measured thermoelectric power of the material/system, without correction to the wire contribution.[2] In many oxides, thermoelectric power of the samples is much greater than that of the leads. For example, according to Cusack and Kendall [33], the magnitude of thermoelectric power of platinum at 1000 K (approximately 727 °C) is approximately $-19.29\,\mu V\,K^{-1}$. The thermoelectric power of GDC10 at 700 °C measured in the present work is $+251.3\,\mu V\,K^{-1}$ (the different sign is due to the minus sign in the Eq. (1)). Thus, Pt

contributes only ~8% to the measured thermoelectric power. This approach of neglecting the thermoelectric power of metallic leads is common when measuring the thermoelectric power of oxides, as discussed by Shahi [9].

To investigate the effect of thermal history of dense and porous samples of GDC10, some of the dense and porous samples were annealed at 1200 °C prior to measurements of thermoelectric power. Then, thermoelectric power was measured at 500 °C, and the sample was cooled to room temperature. The following day, another measurement was made on the same samples at 500 °C. Fig. 4 illustrates this measurement procedure.

3. Results and discussion

3.1. Thermoelectric power of silver

Fig. 5 shows EMF as a function of time on dense and porous samples of silver. The corresponding measured thermoelectric power was -7.8 to $-9.5\,\mu V\,K^{-1}$ for the dense sample, and -8.3 to $-10\,\mu V\,K^{-1}$ for the porous sample. Because silver has the
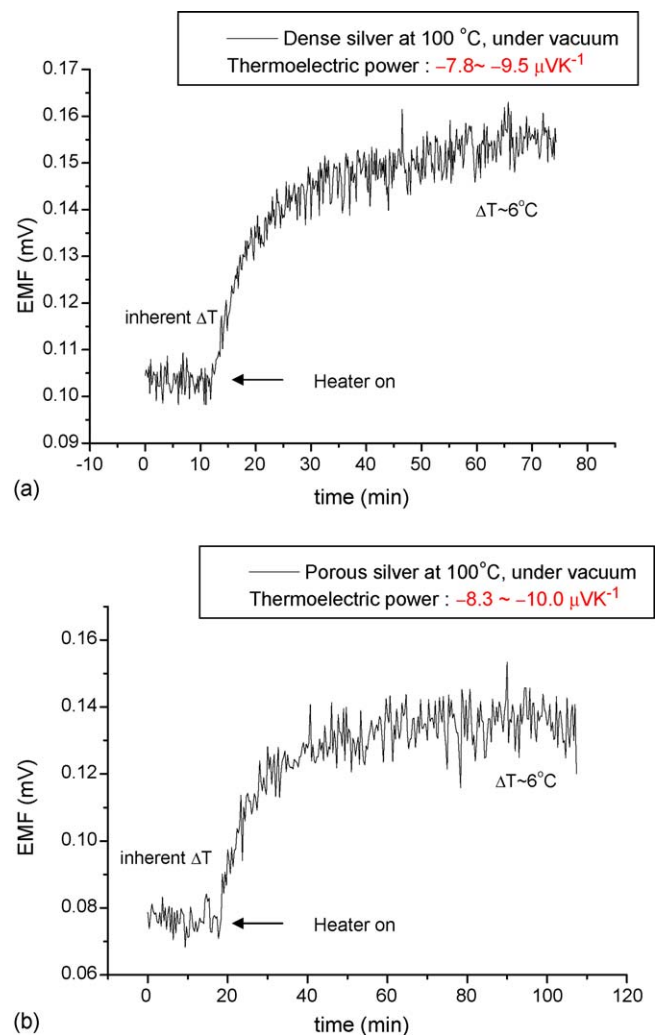

Fig. 5. EMF measurement on: (a) dense silver sample and (b) porous silver sample at two different ΔTs, as a function of time at ~100 °C in vacuum. Note that the thermoelectric power of dense and porous silver is the same.

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[2] It is customary to maintain the average temperature fixed in a typical measurement. In the present work, this aspect was ignored. That is, as the cold end temperature was fixed, the actual average temperature was $T \approx T_{coldend} + (\Delta T)/2$.

highest electrical conductivity of any metal, expectations were that thermal equilibration would occur rapidly under vacuum. However, as shown in Fig. 5(a) and (b), the time required for thermal equilibration, t_{eq}^T, is ~15 min. This relatively long equilibration time is attributed to the thermal inertia of the system, which is mainly related to heat transfer from the surroundings to the sample. Thus, the equilibration time, t_{eq}^T, is on the order of a few minutes, consistent with expectations (based on thermal inertia considerations). The measured thermoelectric power on dense and porous silver is also about the same. Note that the thermoelectric power of silver samples was determined without correction to the Pt wire contribution. However, since the thermoelectric power of silver is rather small, the relative effect of the leads is large. For example, according to Cusack and Kendall [33], the thermoelectric power of pure silver at 400 K (~127 °C) is +2.08 μV K^{-1}, which is different from the value obtained in this work (again, the different sign is due to the minus sign in the Eq. (1)). In such case, correction is necessary if the objective is to measure accurate absolute value of thermoelectric power, which was not the objective in the present work.

3.2. Thermoelectric power of GDC10

Fig. 6(a) shows the results of EMF measurements on a porous sample of GDC10 in air at 700 °C. The EMF was stable before power was supplied to the platinum heater, and it rapidly changed and equilibrated upon the application of a temperature difference across the sample. The particle size (radius), r, in the porous GDC10 sample was on the order of a micron. No information could be found on the chemical diffusion coefficient of oxygen, $\tilde{D}_O$, in this material at 700 °C ($\tilde{D}_O$ only at 900 and 1000 °C was reported [34]). However, at 700 °C, the tracer diffusion coefficient of oxygen, D_O^*, is reported to be on the order of 5×10^{-8} cm^2 s^{-1} [35]. For a material predominant electronic conduction, such as La$_{1-x}$Sr$_x$CoO$_{3-\delta}$, the relation between the chemical diffusion coefficient and the vacancy diffusion has been reported [36,37]. Although GDC is a mixed ionic electronic conductor, this relation was used in order to obtain an approximate estimate of the thermodynamic factor for GDC. Using the oxygen non-stoichiometry data of GDC10 [38], the thermodynamic factor for GDC10 was calculated, which was less than 100. Since the obtained thermodynamic factor is approximate, a value of 100 was assumed in this paper (in many oxides, thermodynamic factors well in excess of 100 have been reported). Thus, assuming a thermodynamic factor of 100, the chemical diffusion coefficient of oxygen, $\tilde{D}_O$, is estimated to be on the order of 5×10^{-6} cm^2 s^{-1}. The approximate time required for composition equilibration, $r^2/\tilde{D}_O$, is estimated as ~0.002 s at a partial pressure of oxygen of ~0.21 atm and at 700 °C. Note that even if the thermodynamic factor is much smaller (say unity), the time required for equilibration is still rather small. That is, the composition equilibration is expected to occur very rapidly in the porous sample. The average measured thermoelectric power is ~0.25 mV K^{-1}. The observation that EMF equilibration required a few minutes again implies that the time required for thermal equilibration, which is on the order of a few minutes,
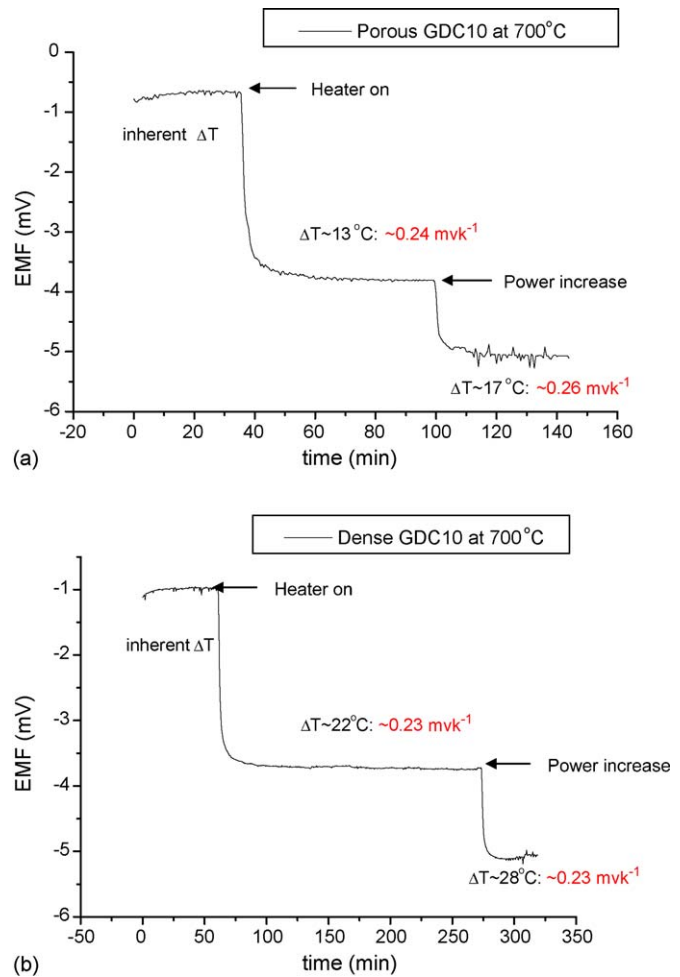

Fig. 6. EMF measurement as a function of time at 700 °C in air: (a) a porous GDC10 sample and (b) a dense GDC10 sample.

is much greater than that required for composition equilibration, i.e., $t_{eq}^T >> t_{eq}^C \approx r^2/\tilde{D}_O$.

In the case of the dense sample of GDC10 also, the EMF equilibrated in a short time, and the measured thermoelectric power was very close to that of the porous sample as shown in Fig. 6(b). The thickness of the dense sample, $2d$, was about 1 mm. Using the same diffusion coefficient at 700 °C, $\tilde{D}_O \sim 5 \times 10^{-6}$ cm^2 s^{-1}, the composition equilibration time, $d^2/\tilde{D}_O$, is about 8 min. This shows that at 700 °C, equilibration is rather rapid in a dense sample as thick as ~1 mm, which is attributed to relatively fast oxygen transport. At a high temperature such as 700 °C, due to the high value of diffusion coefficient of oxygen, the composition equilibration occurred fast also in a dense body; consequently, the measured thermoelectric power was about the same for dense (~0.23 mV K^{-1}) and porous (~0.25 mV K^{-1}) samples.

EMF measurements were also conducted at a lower temperature, 500 °C. Fig. 7 shows that EMF equilibration in the porous sample of GDC10 at 500 °C is quite fast. At 500 °C, the tracer diffusion coefficient of oxygen is reported as -10^{-9} cm^2 s^{-1} [35]. Again, assuming a thermodynamic factor of 100, the chemical diffusion coefficient of oxygen at 500 °C, $\tilde{D}_O$, is estimated as $\sim 10^{-7}$ cm^2 s^{-1}. Assuming that the particle size (radius) in the
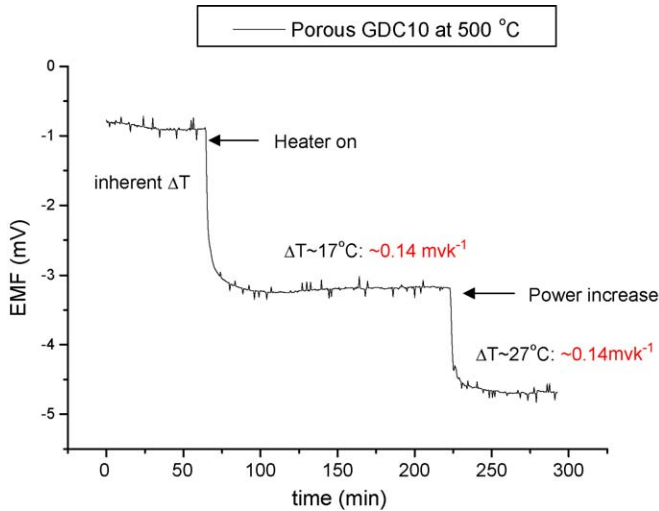
Fig. 7. EMF as a function of time for porous GDC10 at 500 °C in air. Note the rapid EMF equilibration.

porous GDC10 sample was on the order of a micron, the time for compositional equilibration is estimated to be about 0.1 s. If the thermodynamic factor were much smaller, say close to unity, the estimated equilibration time would have been about 10 s. Thus, the compositional equilibration occurs very fast even at a low temperature such as 500 °C, and the thermal equilibration time dominates the total equilibration time for the porous sample, i.e., $t_{eq}^T >> r^2/\tilde{D}_O$.

Fig. 8(a) shows the results of a similar experiment on a dense sample of GDC10 at 500 °C. Note that the EMF did not equilibrate even after 500 min after the application of a small temperature differential, even when initially the EMF appeared to have stabilized. The measurement was repeated on the same sample as shown in Fig. 8(b). Although EMF equilibration was not achieved, power to the platinum heater was supplied to establish a temperature difference across the sample. Contrary to the case of the porous sample, EMF increased initially, and then slowly decreased as the composition equilibrated. The corresponding estimated thermoelectric power was ~0.024 mV K^{-1}, which is quite different from that obtained on the porous sample, ~0.14 mV K^{-1}. Also, as the EMF had not equilibrated, the thermoelectric power measured on the dense sample is clearly not accurate. At 500 °C, using $\tilde{D}_O \sim 10^{-7}$ cm^2 s^{-1}, the estimated time for compositional equilibration in a 1 mm thick dense sample is ~7 h, which is much greater than ~0.1 s for porous samples. The observed, extremely slow kinetics of equilibration in the dense sample is consistent with the estimated sluggish kinetics.

Let us suppose that a typical experiment on thermoelectric power measurement on a porous sample is conducted for 2 h. Let us assume that particle radius in the porous sample is r. The chemical diffusion coefficient of oxygen may be given as:

$$\tilde{D}_O \approx D_0 \exp\left[\frac{-Q}{RT}\right] \tag{2}$$

where Q, R and T are the activation energy, the gas constant and the measurement temperature, respectively. In terms of the time
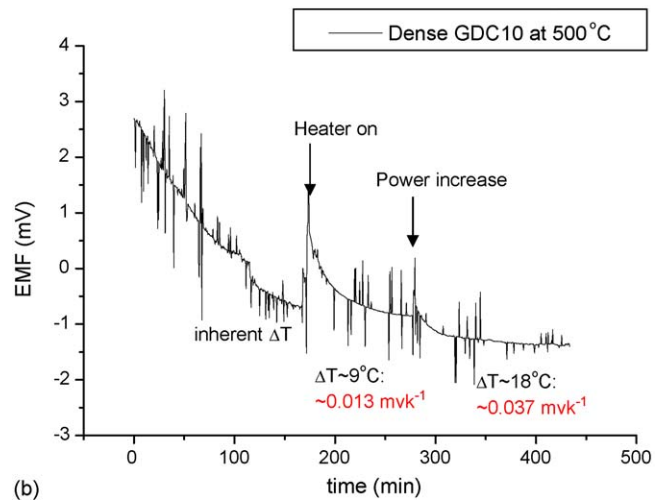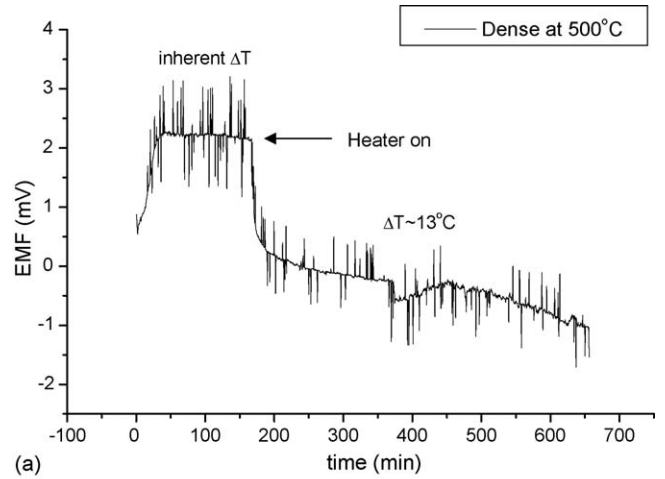

Fig. 8. (a) EMF measurement on dense GDC10 as a function of time at 500 °C in air. (b) Note that a different result was obtained using the same sample.

required for compositional equilibration, namely, t_{eq}^C, the chemical diffusion coefficient may be written as $\tilde{D}_O \approx r^2/t_{eq}^C$. Thus, the minimum temperature, T_{min}, above which it is possible to measure thermoelectric power using a porous sample of particle size r is given by

$$T_{min} \approx \frac{Q}{R \ln((t_{eq}^C D_0)/r^2)} \tag{3}$$

in a prescribed t_{eq}^C. Because the experimental duration depends on the time required for composition equilibration to occur, t_{eq}^C in Eq. (3) is set at 2 h. Assuming that the activation energy, Q, and pre-exponent, D_0, are 100 kJ mol^{-1} and 10^{-1} cm^2 s^{-1}, respectively, the minimum temperature, T_{min}, is estimated as ~455 K or ~182 °C. In other words, for the experiment duration of 2 h (or for the compositional equilibration to occur within 2 h), the measurement should be conducted above 182 °C. Thus, the minimum measurement temperature for the specific measurement time can be estimated from Eq. (3). It is readily seen that the use of porous samples makes it possible to conduct measurements of thermoelectric power at rather low temperatures. If we need
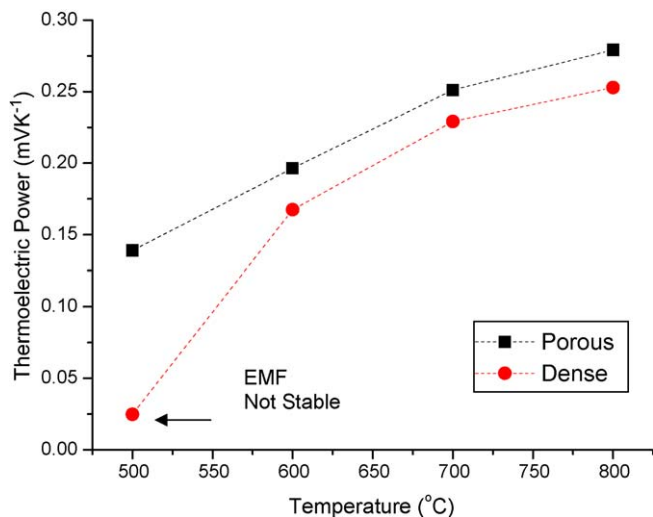
Fig. 9. Thermoelectric power of GDC10 measured on porous and dense samples as a function of temperature (500–800 °C) in air.

to conduct the measurements at even lower temperatures, the particle size should be decreased to ensure faster compositional equilibration, or the experimental duration should be increased. However, the particle size should not be too fine, i.e., it should not be in the nano regime. This is because if the particle size is too fine, a significant fraction of atoms will be on the surface. In such a case, measurements may not be representative of equilibrated bulk samples, but may include 'nano' effects. Additionally, there may likely be changes in defect concentrations due to space charge effects and/or due to adsorption of gaseous species. This suggests that the particle size should be in the micron range, but not in the nano size range.

Fig. 9 compares thermoelectric power measured on dense and porous samples of GDC10 in air. These data show that the measured thermoelectric power on the dense sample above 600 °C is essentially the same as that measured on the porous sample, consistent with expectations based on $\tilde{D}_O$. However, considerable difference is evident between measurements made on dense and porous samples at 500 °C. The measurements at 500 °C on the dense sample are not reliable due to slow equilibration kinetics.

3.3. Heat treatments on dense and porous samples of GDC10 effect of thermal history

Measurements thus far conducted indicate that the results of EMF measurements on dense samples of BCN18 as well as GDC10 varied from measurement to measurement, especially at low temperatures below 600 °C [32]. Dense samples sometimes appeared to have equilibrated quickly, although the measured thermoelectric power was usually not reproducible—and thus believed to be incorrect. The assumption is that under such conditions, only thermal equilibration occurred, but not the compositional equilibration. In some earlier work on Mg-stabilized zirconia, it was observed that the thermoelectric power changed substantially after thermal cycling [39]. This discrepancy may be related to the thermal history wherein the sample did not equilibrate under the imposed conditions of atmosphere and tem-
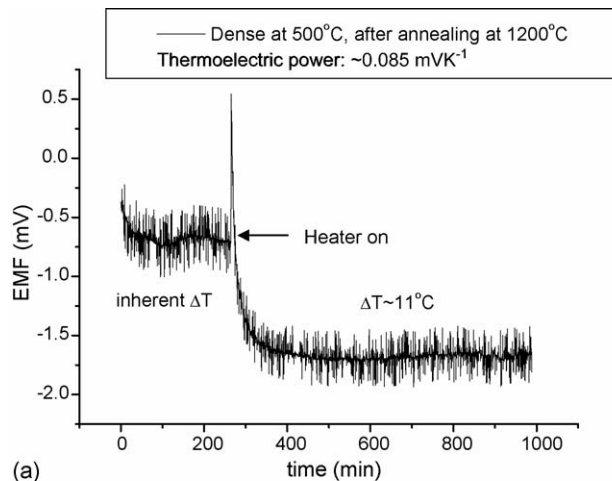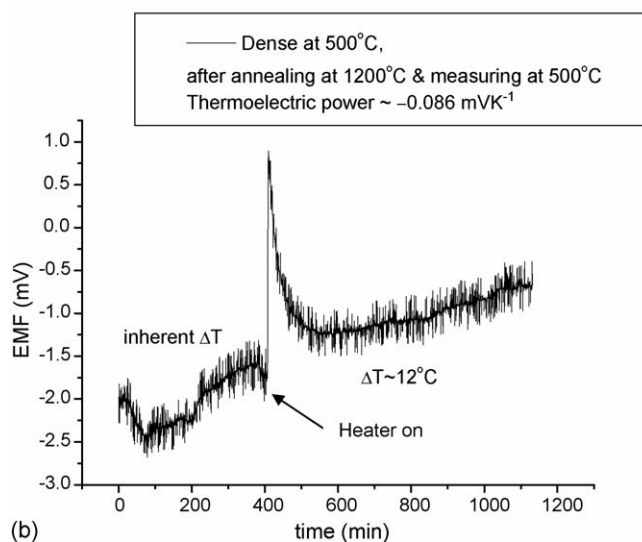
Fig. 10. EMF vs. time for dense GDC10 at 500 °C in air. (a) Measurement on the dense GDC10 sample after annealing at 1200 °C, and (b) the second measurement conducted on the same sample the next day. Note the effect of thermal history on measurements.

perature. This must be related to slow kinetics of equilibration in a dense sample, associated with slow diffusion. In porous samples, compositional equilibration is expected to occur rapidly. It is thus the expectation that porous samples should not exhibit thermal history. That is, at sufficiently high temperatures, the thermoelectric power measured on porous samples should not exhibit thermal history, unlike dense samples. In order to explore this possibility, the following experiments were conducted.

The EMF measurements on a dense sample of GDC10 are shown in Fig. 10 as a function of time at 500 °C. Fig. 10(a) shows results of a measurement conducted at 500 °C after an annealing treatment at 1200 °C. The sample appeared to equilibrate, and the measured thermoelectric power was ~0.085 mV K^{-1}. The sample was subsequently cooled to room temperature, and then reheated back to 500 °C for another measurement. The results of this measurement are shown in Fig. 10(b). Note that the EMF did not equilibrate over the duration of the experiment. Nevertheless, a measurement of thermoelectric power was conducted. The measured thermoelectric power was quite different- it was
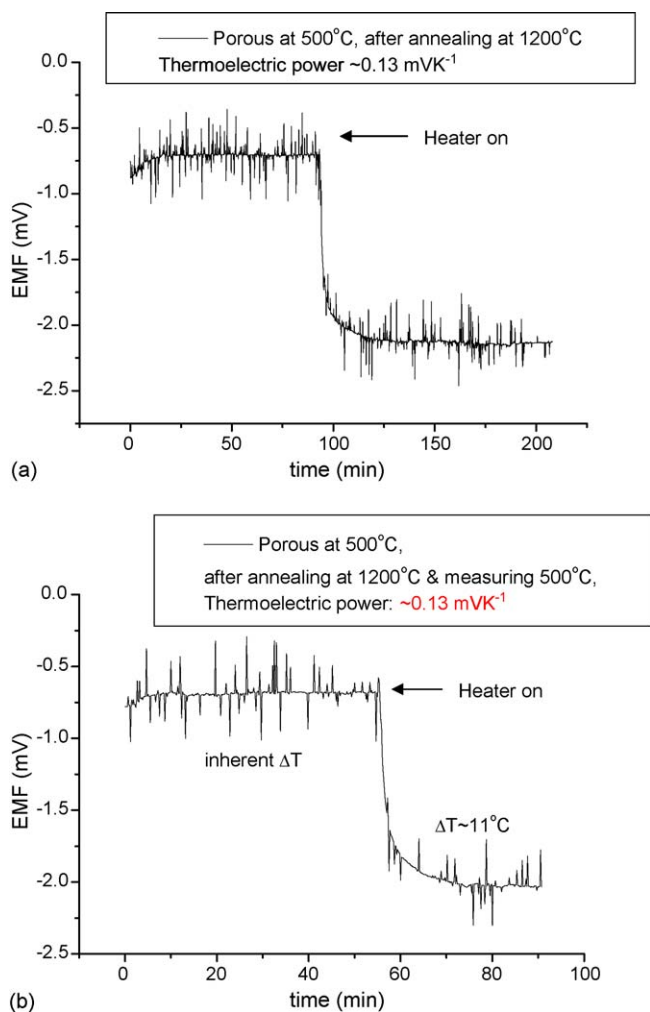
Fig. 11. EMF vs. time for porous GDC10 at 500 °C in air. (a) Measurement on the porous GDC10 sample after annealing at 1200 °C, and (b) the second measurement conducted on the same sample the next day. Note that the measurements are not dependent on thermal history.

approximately −0.086 mV K^{-1} (note the negative sign), that is, it even exhibited a different sign. This is due to the thermal history effect, which shows that the measured thermoelectric power on dense samples is inaccurate and unreliable. The effect of Pt lead correction, however, is very small ($\sim$19 μV K^{-1}) compared to the thermoelectric power of GDC10. Also, the Pt correction should be the same in both cases, since Pt leads do equilibrate, but the sample does not. For this reason, the observed variation in the measured thermoelectric power on dense samples is attributed to the fact that the sample did not equilibrate during the course of the measurement. Both of these measurements must be regarded as unreliable, and the result of slow compositional equilibration kinetics.

Similar measurements were conducted on a porous sample of GDC10. Fig. 11(a) shows results of a measurement conducted at 500 °C after an annealing treatment at 1200 °C. The sample equilibrated rapidly, and the measured thermoelectric power was $\sim$0.13 mV K^{-1}. The sample was subsequently cooled to room temperature, and then reheated back to 500 °C for another measurement. The results of this measurement are shown in

Fig. 11(b). Note that the sample again equilibrated very quickly. Also, the measured thermoelectric power was $\sim$0.13 mV K^{-1}, essentially the same as in Fig. 11(a). That is, the thermoelectric power measured on porous GDC10 is not subject to thermal history effects (for measurement above at least 500 °C), consistent with expectations based on rapid equilibration kinetics. Thus, the measured thermoelectric power on porous GDC10 at 500 °C should be representative of true material/environment parameter, unlike measurements on dense GDC10.

4. Summary

The present work demonstrates that measurements of thermoelectric power on GDC10 using porous samples are more reproducible, and thus presumed to be more accurate than those made using dense samples, especially at low temperatures where the kinetics of compositional equilibration can be rather sluggish. In order to investigate the effect of thermal history, thermoelectric power measurements were conducted on dense and porous samples subjected to various thermal treatments. It was observed that the measured thermoelectric power in porous samples was independent of thermal history (for measurement above at least 500 °C), as long as the measurement conditions (temperature and atmosphere) were identical. By contrast, measured thermoelectric power on dense samples was influenced by thermal history. Thus, especially at low temperatures ($\sim$500 °C), the thermoelectric power measurements on dense GDC10 are deemed incorrect and unreliable. The present work suggests that porous rather than dense samples should be used for thermoelectric power measurements on oxides. The same general conclusion is expected to be valid for other materials, in which compositional equilibration by interaction with the atmosphere occurs upon change of measurement conditions.

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References

[1] R.R. Heikes, R.W. Ure, Thermoelectricity: Science and Engineering, Interscience Publishers, New York, 1961.
[2] J. Chaussy, A. Guessous, J. Mazuer, Rev. Sci. Instrum. 52 (11) (1981) 1721.
[3] E.R. Rumbo, J. Phys. F: Metal Phys. 6 (1976) 85.
[4] M. Ewbank, J.L. Imes, W.P. Pratt Jr., P.A. Schroeder, J. Tracy, Phys. Lett. 59A (1976) 316.
[5] N. Wendling, J. Chaussy, J. Mazuer, J. Appl. Phys. 73 (6) (1993) 2278.
[6] H.Y. Yu, W.F. Leonard, J. Appl. Phys. 44 (1973) 5324.
[7] A.M. Guenault, D.G. Hawksworth, J. Phys. F: Metal Phys. 7 (1977) L219.
[8] R.E. Howard, A.B. Lidiard, Discuss. Faraday Soc. 23 (1957) 113.
[9] K. Shahi, Phys. Status Solidi 11 (1977) A41.
[10] A. Trestman-Matts, S.E. Dorris, T.O. Mason, J. Am. Ceram. Soc. 66 (1983) 589.
[11] E.O. Ahlgren, J. Phys. Chem. Solids 58 (1997) 1475.
[12] E.O. Ahlgren, F.W. Poulsen, J. Phys. Chem. Solids 57 (1995) 589.
[13] V.I. Tsidilkovski, V.P. Gorelov, V.B. Balakireva, Solid State Ionics 162–163 (2003) 55.
[14] A. Tschope, S. Kilassonia, B. Zapp, R. Birringer, Solid State Ionics 149 (2002) 261.

[15] E.O. Ahlgren, J. Ranlov, F.W. Poulsen, J. Electrochem. Soc. 142 (1995) 4230.
[16] E.O. Ahlgren, Solid State Ionics 97 (1997) 489.
[17] E.O. Ahlgren, F.W. Poulsen, Solid State Ionics 86–88 (1996) 1173.
[18] K. Amezawa, S. Kjelstrup, T. Norby, Y. Ito, J. Electrochem. Soc. 145 (1998) 3313.
[19] E.B. Mitberg, M.V. Patrakeev, I.A. Leonidov, V.L. Kozhevnikov, K.R. Poeppelmeier, Solid State Ionics 130 (2000) 325.
[20] T. Ohtani, K. Ohkuma, Solid State Commun. 72 (1989) 767.
[21] T. Bak, J. Nowotny, C.C. Sorrell, M.F. Zhou, J. Mater. Sci. 15 (2004) 645.
[22] C.B. Alcock, K. Fitzner, K.T. Jacob, J. Chem. Thermodyn. 9 (1977) 1011.
[23] E.O. Ahlgren, F.W. Poulsen, Solid State Ionics 70–71 (1994) 528.
[24] S.K. Ratkje, Y. Tomii, J. Electrochem. Soc. 140 (1993) 59.
[25] E.O. Ahlgren, F.W. Poulsen, Solid State Ionics 82 (1995) 193.
[26] H.I. Yoo, J.H. Hwang, J. Phys. Chem. Solids 53 (1992) 973.
[27] Z. Takehara, K. Kanamura, S. Yoshioka, J. Electrochem. Soc. 136 (1989) 2506.
[28] J.D. Hodge, H.K. Bowen, J. Am. Ceram. Soc. 64 (1981) 431.
[29] J. Janek, C. Korte, Solid State Ionics 92 (1996) 193.
[30] M. Vennekamp, J. Janek, Solid State Ionics 118 (1999) 43.
[31] C. Wagner, Prog. Solid State Chem. 7 (1972) 1.
[32] H. Lim, A.V. Virkar, J. Electrochem. Soc., submitted for publication.
[33] N. Cusack, P. Kendall, Proc. Phys. Soc. 72 (1958) 898.
[34] M. Katsuki, S. Wang, K. Yasumoto, M. Dokiya, Solid State Ionics 154–155 (2002) 589.
[35] E. Ruiz-Trejo, J.D. Sirman, Yu.M. Baikov, J.A. Kilner, Solid State Ionics 113–115 (1998) 565.
[36] J. Mizusaki, J. Tabuchi, T. Matsuura, S. Yamauchi, K. Fueki, J. Electrochem. Soc. 136 (1989).
[37] L.M. van der Harr, M.W. den Otter, M. Morskate, H.J.M. Bouwmeester, H. Verweij, J. Electrochem. Soc. 149 (3) (2002) J41–J46.
[38] S. Wang, H. Inaba, H. Tagawa, M. Dokiya, T. Hashimoto, Solid State Ionics 107 (1998) 73.
[39] M. Sasabe, X.F. Song, Tetsu to Hagane 76 (1990) 545.