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## Short communication

## Hot-pressed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub>

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## ABSTRACT

The electrical and mechanical properties of hot-pressed versus sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> at temperature of 1050 °C were investigated. It was observed that hot-pressed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> exhibited a higher total Li-ion conductivity (~20×) and hardness (~11×) compared to sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> as a result of its higher density. Hot-pressed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> and a similar relative density and total Li-ion conductivity when compared to Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> sintered at 1250 °C, where significant Li<sub>2</sub>O loss occurs. These results suggest that hot-pressing can be used as a consolidation method to reduce Li<sub>2</sub>O loss to obtain dense Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub>.

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#### 1. Introduction

Recently, there has been interest in the development of Li-air batteries for high energy applications. One configuration involves the use of a Li anode in a non-aqueous electrolyte which is separated from an aqueous electrolyte containing the air cathode by a solid state Li-ion conducting membrane [1–5]. One of the requirements for the membrane besides chemical stability, is high Li-ion conductivity, which has resulted in interest in the use of doped-LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (LTP) as a potential membrane [1–5]. Besides doped-LTP, lithium lanthanum titanates, Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub>, (LLTO) having a perovskite structure are also under consideration as possible membrane materials because, of their chemical stability and high Li-ion conductivity [6–9]. If lithium lanthanum titanates are to be used as possible membrane materials for Li-air batteries a dense material is required. One of the problems with LLTO is high temperature sintering (>1250 °C [9–11]) is required to achieve high densities (relative density >95%). The high sintering temperature results in Li<sub>2</sub>O loss leading to problems in controlling Li-ion content and hence, ionic conductivity. One possible solution to achieve high density LLTO and overcome Li<sub>2</sub>O loss is to hot-press LLTO at a temperature lower than what is typically used in conventional sintering. Achieving the same relative density at a lower temperature using hot-pressing compared to conventional sintering is possible since, during hot-pressing the applied stress adds an additional driving force for densification which is about 10–20 times the capillary driving force associated with conventional sintering [13,14].

The purpose of this paper is to report on some of the first electrical and mechanical properties of  $Li_{0.33}La_{0.57}TiO_3$  hot-pressed at a temperature of 1050 °C, which is ~175–200 °C lower than that typically used to sinter  $Li_{0.33}La_{0.57}TiO_3$ , where no significant  $Li_2O$  loss occurs [11]. The properties will also be compared to  $Li_{0.33}La_{0.57}TiO_3$  sintered at 1050 °C and higher temperatures. At present there is no information on the mechanical properties of  $Li_{0.33}La_{0.57}TiO_3$ . Such information is needed if  $Li_{0.33}La_{0.57}TiO_3$  is to be used as a membrane in Li–air batteries.

### 2. Experimental

#### 2.1. Material preparation

Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> was chosen since, this composition has one of the highest reported bulk Li-ion conductivities of the lithium lanthanum titanates [9,15]. Stoichiometric amounts of La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> (anatase), and Li<sub>2</sub>CO<sub>3</sub> were mixed. The mixture was then heated in air at 10°Cmin<sup>-1</sup> to 800°C and held for 4 h before ramping at 10°Cmin<sup>-1</sup> to 1100°C and held for 36 h before cooling to room temperature at 10°Cmin<sup>-1</sup>.

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ntensity (arb. units)

#### 2.2. Consolidation

The Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> powders were hot-pressed in a graphite die lined with graphfoil which was then heated to 1050°C at which time a stress of 70 MPa was applied and held for a period of 1.5 h after which the load was removed and sample cooled to room temperature. During the heating and cooling stages the furnace was flushed with flowing argon. The hot-pressed specimen was disc shaped with a thickness of about  $\sim 11$  mm and a diameter between 22 and 23 mm. Rectangular parallelepiped specimens of about  $5 \text{ mm} \times 5 \text{ mm} \times 3 \text{ mm}$  were cut from the hot-pressed disc using a low-speed diamond saw for microstructural analysis, density, electrical and mechanical property measurements. For sintering the Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> powders were first uniaxially pressed into cylindrical specimens 13 mm in diameter with a thickness between 2 and 4 mm at pressure of 200 MPa. A 3 wt.% polyvinyl alcohol binder was used. The pellets were then sintered at 1050 °C for 1.5 h under air on platinum foil.

#### 2.3. Property characterization

The bulk density of the sintered and hot-pressed samples was determined from the weight and physical dimensions and also by the Archimedes method using methanol as the immersion fluid. The relative density values were determined by dividing the bulk density by the Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> theoretical density. The microstructure of the sintered and hot-pressed samples was examined using a scanning electron microscope (SEM) on samples that were polished and thermally etched at 950 °C for 2 h under air.

The Li content of the Li<sub>0 33</sub>La<sub>0 57</sub>TiO<sub>3</sub> samples prior to and after hot-pressing/sintering was determined using inductively coupled plasma analysis (Galbraith Laboratories, Inc., Knoxville, TN).

AC and DC room temperature electrical conductivity measurements were performed on sintered and hot-pressed samples using the two probe method. Au was sputter coated on to the top and bottom surfaces of the specimens. AC measurements were undertaken to determine ionic conductivity. AC impedance was measured using a Solatron 1260 Impedance Analyzer in the frequency range 1–10<sup>6</sup> Hz. DC measurements were undertaken to determine electronic conductivity. DC resistances were measured using a Keithly 6517A Electrometer/High Resistance Meter with a Model 8009 Resistivity Test Fixture capable of measuring volume resistivties as high as  $10^{18} \Omega$  cm.

The mechanical properties of the sintered and hot-pressed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> materials were evaluated from microhardness measurements. Microhardness was chosen to characterize the mechanical properties of the sintered and hot-pressed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> materials for the following reasons: (1) hardness is related to strength and (2) due to small volume of material and ease of specimen preparation and testing [16,17]. The room temperature Vickers hardness of polished sintered and hot-pressed specimens was measured at a load of 9.8 N at an indentation time of 15 s.

#### 3. Results and discussion

#### 3.1. Color

The sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> disc was white colored like the original starting powders. The color of the hot-pressed samples was blue on the surface, indicating reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> had occurred on the surface as a result of the carbon foil and reducing atmosphere [3]. In order to convert the surface  $Ti^{3+}$  back to  $Ti^{4+}$ all hot-pressed samples were heated at 900 °C for 2 h under air. It was found that after this heat-treatment that all samples were col-

100 30 60 80 20 40 50 70 2-theta Fig. 1. X-ray diffraction pattern of Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub>.

ored white throughout the total thickness. All hot-pressed samples were given this additional annealing step prior to microstructural analysis, density, conductivity and hardness measurements.

Inductively coupled plasma analysis revealed no significant Li loss during heat-treatment. The actual Li content of the calcined  $Li_{0.33}La_{0.57}TiO_3$  powder was  $0.333 \pm 0.01$ , after hot-pressing and annealing,  $0.331 \pm 0.01$  and after sintering  $0.332 \pm 0.01$ . These results are in agreement with data of Ban and Choi [11], who revealed negligible Li loss for sintering below 1100 °C for LLTO of compositions; Li<sub>0.30</sub>La<sub>0.57</sub>TiO<sub>3</sub> and Li<sub>0.35</sub>La<sub>0.57</sub>TiO<sub>3</sub>. However, at temperatures >1250 °C Ban and Choi [11] observed that the lithium content rapidly decreased.

#### 3.2. Structure

The X-ray diffraction pattern for the Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> powder prior to sintering is shown in Fig. 1 (Cu  $K_{\alpha}$  radiation). From Fig. 1 it can be seen that the powder is single phase. All peaks have been indexed to a perovksite structure with the tetragonal P4/mmm space group [8,9,18]. The tetragonal structure results from doubling of the cubic perovskite cell along the *c*-axis. The peaks associated with the superstructure are annotated with an inverse triangle. The X-ray patterns of the sintered and hot-pressed annealed and materials were similar to that shown in Fig. 1, suggesting that no change in structure occurred during the consolidation step.

#### 3.3. Density

The true density of the LLTO sintered sample is  $3.2591\pm 0.094\,g\,cm^{-3}$  while it is  $4.7132\pm 0.094\,g\,cm^{-3}$  for the hot-pressed and annealed sample. The relative density (measured/theoretical) of the sintered and hot-pressed and annealed  $Li_{0.33}La_{0.57}TiO_3$  samples is  $65 \pm 2\%$  and  $94 \pm 2\%$ , respectively. The values based on the physical dimensions and weight are in close agreement with those determined using the Archimedes method. The relative density of sintered  $Li_{0.33}La_{0.57}TiO_3$  (65±2%) is in agreement with the value of ~58% predicted for a sintering temperature of 1050 °C (2 h) using the data from Ban and Choi [11] and ~64% 1050 °C (8 h) using data from Yang et al. [18]. The relative density of the hot-pressed sample is  $1.5 \times$  that for the sintered sample. The higher density of the hot-pressed sample compared to the sintered sample is expected because the addition of the applied stress during hot-pressing increases the driving force for densification over that for conventional sintering [12,13,14]. In order to achieve a relative density of 94% Ban and Choi [11] needed to sinter  $Li_{0.35}La_{0.57}TiO_3$  at a temperature of  $1250\,^\circ\text{C}$  for 2h whereas Yang et al. [18] needed to sinter Li<sub>0.35</sub>La<sub>0.57</sub>TiO<sub>3</sub> at





Fig. 2. Scanning electron micrograph of sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub>.

a temperature of 1225 °C for 8 h to achieve a relative density of ~94%. At 1250 °C significant loss of Li<sub>2</sub>O was observed [11]. In contrast, the hot-pressed sample required only to be heated to 1050 °C (175–200 °C lower than the sintering temperature of Yang et al. [18] and Ban and Choi [11], respectively) to achieve a similar relative density. Below 1100 °C negligible Li loss for sintering was observed [11].

#### 3.4. Microstructure

SEM micrographs of the sintered and hot-pressed and annealed  $Li_{0.33}La_{0.57}TiO_3$  thermally etched samples are shown in Figs. 2 and 3, respectively. A comparison of Figs. 2 and 3 shows that the sintered sample is much more porous than the hot-pressed sample, as expected based on the relative density measurements. Both the sintered and hot-pressed and annealed samples have grains that are fairly equiaxed. The grain size is about the same for



Fig. 3. Scanning electron micrograph of hot-pressed and annealed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub>.

both samples,  $\sim 1-2 \,\mu$ m. A similar grain size is expected since; both samples were exposed to the same high temperature (1050 °C) for the same time (1.5 h).

#### 3.5. Electronic conductivity

The electronic conductivity of the sintered and hot-pressed and annealed sample is  $3 \times 10^{-9}$  and  $4 \times 10^{-9}$  S cm<sup>-1</sup>, respectively. These values are in good agreement with each other. This is expected since, the sintered and hot-pressed powders come from the same source (i.e., have the same background impurities) and had nearly the same heat-treatment (one sintered under air and the other annealed under air). These values are in agreement with the reported electronic conductivity values for Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> at room temperature of  $5 \times 10^{-9}$  to  $1 \times 10^{-8}$  S cm<sup>-1</sup> [15].

#### 3.6. *Ionic conductivity*

The room temperature AC conductivity results for the hotpressed and annealed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> samples using Li-ion blocking Au electrodes are shown in the full complex impedance plot in Fig. 4. From Fig. 4 several important points are observed. Firstly, the data separates into a high frequency region which contains a semicircle and low frequency region which contains a spike. For this case, since we have Li blocking electrodes the shape of the curve represents a material which is predominately a Li-ion conductor with very low electronic conductivity [19–21]. Secondly, the low frequency intercept of the semicircle on the Z' axis gives the total ionic resistance, which includes the contribution of the lattice and the grain boundary components [20–22]. Using this resistance and sample dimensions the total ionic conductivity of the sintered and hot-pressed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> samples was calculated. The total ionic conductivity of the hot-pressed and annealed sample is  $6 \times 10^{-6}$  S cm<sup>-1</sup>. The complex impedance plot for the sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> sample looked similar to that shown in Fig. 4, in that the data separates into a high frequency region which contains a semicircle and low frequency region which exhibits a spike. Using the low frequency intercept of the semicircle on the Z' axis and sample dimensions the total ionic conductivity of the sintered  $Li_{0.33}La_{0.57}TiO_3$  sample was determined to be  $3 \times 10^{-7}$  S cm<sup>-1</sup>. The total ionic conductivity of the hot-pressed and annealed sample is  $\sim$ 20× higher than that of the sintered sample. These results are in agreement with the hot-pressed versus sintered NASICON results of Zhu et al. [23], who observed about a factor of 2 increase in total



Fig. 4. Complex impedance plot of hot-pressed and annealed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub>.



Fig. 5. High frequency region of the complex impedance plot of hot-pressed and annealed  $Li_{0.33}La_{0.57}TiO_3$ .

ionic conductivity for the hot-pressed material compared to the sintered material and the very recent results of Wolfenstine et al. [3] for LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, who observed about a factor of 5 increase in total conductivity for the hot-pressed material compared to the sintered material.

A blow-up of the high frequency end of the semi-circle shown in Fig. 4 is shown in Fig. 5. The low frequency intercept of this semicircle on the Z' axis gives the Li-ion lattice conductivity [19,20,22,24]. Using this resistance and sample dimensions the lattice conductivity of the hot-pressed and annealed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> samples was calculated. The value of the Li-ion lattice conductivity for the hot-pressed and annealed sample is  $1 \times 10^{-3}$  S cm<sup>-1</sup>. The sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> sample gave a similar curve, which yielded a Liion lattice conductivity  $9 \times 10^{-4}$  S cm<sup>-1</sup>. Both the hot-pressed and annealed and sintered samples have the same value for the Li-ion lattice conductivity. This is expected since, the sintered and hotpressed powders come from the same source (i.e., have the same background impurities) and had nearly the same heat-treatment (one sintered under air and the other annealed under air). This value of the Li-ion lattice conductivity is in good agreement with the Li-ion lattice conductivity of Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> [7–9,15,18].

A comparison of the lattice conductivity ( $\sim 1 \times 10^{-3} \, \text{S cm}^{-1}$ ) with the total conductivity, lattice plus grain boundary ( $3 \times 10^{-7} \, \text{S cm}^{-1}$  for the sintered material;  $6 \times 10^{-6} \, \text{S cm}^{-1}$  for the hot-pressed and annealed material), confirms what has been suggested in the literature [18,24–28], in that the ionic conductivity of polycrystalline materials is controlled by the lower conductivity grain boundaries. Furthermore, since the lattice conductivity of both hot-pressed and annealed and sintered material is the same, the higher total conductivity for the hot-pressed and annealed material must be due to a difference in the conductivity of the grain boundary component between these two materials.

The difference in the ionic conductivity of the grain boundary component of the hot-pressed and annealed  $Li_{0.33}La_{0.57}TiO_3$  material compared to the sintered  $Li_{0.33}La_{0.57}TiO_3$  material is related to the higher relative density (i.e., lower porosity) of the hot-pressed material (~94%) versus the sintered material (~65%). It is has been observed that as the density increases (porosity along the grain boundaries decreases) the total ionic conductivity increases as a result of the increase in the conductivity of the grain boundary component [2,4–6,10,21,24]. It has also been shown that as the grain size increases that the total ionic conductivity increases as a result of the increase in the conductivity of the component associated with the grain boundaries [10,11]. From the SEM images shown in Figs. 2 and 3, it can be observed that the hot-pressed sample has less intergranular porosity leading to larger grain boundary area compared to the sintered sample. As a consequence of the higher grain boundary area, the ionic conductivity grain boundary component for the hot-pressed sample is higher than that for the sintered sample. Since, the lattice conductivity of both the sintered and hotpressed samples is the same, the higher total ionic conductivity of hot-pressed sample is a result of its higher grain boundary area (lower intergranular porosity).

The total ionic conductivity of Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> for the sintered sample  $(3 \times 10^{-7} \text{ S cm}^{-1})$  is in good agreement with sintering data of Ban and Choi [11] extrapolated to  $1050 \circ C (\sim 4 \times 10^{-7} S \text{ cm}^{-1})$ and Yang et al. [18] to  $1050 \,^{\circ}$ C ( $\sim 5 \times 10^{-7} \,$ S cm<sup>-1</sup>). In addition, the total conductivity of the hot-pressed and annealed sample  $Li_{0.33}La_{0.57}TiO_3$  ( $6 \times 10^{-6} S cm^{-1}$ ) is close to value of  ${\sim}3\times10^{-6}\,S\,cm^{-1}$  obtained by Ban and Choi [11] for  $Li_{0.33}La_{0.57}TiO_3$ sintered at 1250 °C (200 °C higher than the hot-pressing temperature) compared at the same relative density (~94%). The total ionic conductivity obtained by Yang et al. [18] for Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> at about the same relative density of  $\sim$ 94% was  $\sim$ 5  $\times$  10<sup>-5</sup> S cm<sup>-1</sup>. The results for Yang et al. [18] are an order of magnitude higher than those for the current study and Ban and Choi [11]. Reasons for this discrepancy are not known. However one possible difference could be that the grain size difference between the various studies. The grain size of the current study was between 1 and  $2 \mu m$ , whereas the grain size for the samples of Ban and Choi [11] was around 2 µm, and for Yang et al. [18], the grain size was around 6 µm. As stated earlier, it has been shown that as the grain size increases that the total ionic conductivity increases as a result of the increase in the conductivity of the component associated with the grain boundaries. Thus, it is expected and is observed when comparing the various studies that larger grain size material of Yang et al. [18] had the lower total ionic conductivity.

The ionic transport number (ionic conductivity/total conductivity) for hot-pressed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> is ~1 and for sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> is ~0.99. These results confirm that Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> when heated under oxidizing conditions is an ionic conductor.

#### 3.7. Microhardness

The hardness of the hot-pressed and annealed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> material was  $\sim$ 963 HV. This is about 11 $\times$  that for sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> (~89 HV). There are two major microstructural features that control the hardness of these materials. The first is grain size [13,29-31]. It is known that as grain size increases hardness decreases. Typically it is observed that hardness varies inversely with grain size to the one-half power [29-31]. However, since the grain size for the hot-pressed and annealed and sintered is nearly the same: grain size can be ruled out as a microstructural variable responsible for the difference in hardness between the two materials. The second variable is porosity. Pores reduce the strength of a material by reducing the cross-sectional over which the load is applied and acting as stress concentrators [13,14,16,17]. Hence, it is expected that the hot-pressed and annealed material with its lower porosity (i.e., higher density) versus the sintered material should have the higher hardness. This is in agreement with the experimental results. Thus, the difference in porosity can explain the variation in the hardness values between the two materials.

#### 4. Conclusions

The electrical and mechanical properties of hot-pressed versus sintered  $Li_{0.33}La_{0.57}TiO_3$  at temperature of 1050 °C were investigated. Both materials had a grain size between 1 and  $2\,\mu$ m

however, the relative density of the hot-pressed materials was much greater (~94%) than that of the sintered materials (~65%). The total ionic conductivity of the hot-pressed and annealed sample is ~20× higher than that of the sintered sample. The hardness of the hot-pressed Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> material was ~11× that for sintered Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub>. The higher conductivity and hardness of the hot-pressed material compared to the sintered material is a result of its higher density. The same relative density (~94%) obtained by hot-pressing required Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> to be sintered at a temperature. Hot-pressing was performed at a temperature where no significant Li<sub>2</sub>O loss occurs. Hence, these preliminary results suggest that hot-pressing can be used as a consolidation method to obtain dense Li<sub>0.33</sub>La<sub>0.57</sub>TiO<sub>3</sub> and hence, reduce Li<sub>2</sub>O loss.

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#### References

- [1] I. Kowalczk, J. Read, M. Salomon, Pure Appl. Chem. 5 (2007) 851.
- [2] S.J. Visco, B.D. Katz, Y.S. Nimon, L.C. De Jonghe, US Pat. 7,282,295 B2 (2007).
  [3] J. Wolfenstine, J.L. Allen, J. Sumner, J. Sakamoto, Solid State Ionics 180 (2009)
- 961.
- [4] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, O. Yamamoto, J. Power Sources 189 (2009) 371.
- [5] J.S. Thokchom, B. Kumar, J. Electrochem. Soc. 154 (2007) A331.

- [6] J. Wolfenstine, J.L. Allen, J. Mater. Sci. 43 (2008) 7247.
- [7] V. Thangadurai, W. Weppner, Solid State Ionics 12 (2006) 81.
- [8] Y. Inaguma, L.Q. Chen, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta, M. Wakihara, Solid State Commun. 86 (1993) 689.
- [9] H. Kawai, J. Kuwano, J. Electrochem. Soc. 141 (1994) L74.
- [10] J.G. Kim, H.G. Kim, H.T. Chung, J. Mater. Sci. 18 (1999) 493.
- [11] C.W. Ban, G.M. Choi, Solid State Ionics 140 (2001) 285.
- [12] A. Morata-Orrantia, S. Garcia-Martin, M.A. Alario-Franco, Chem. Mater. 15 (2003) 3991.
- [13] M.V. Barsum, Fundamentals of Ceramics, The McGraw-Hill Companies Inc., New York, 1997.
- [14] Y.M. Chiang, D. Birnie III, W.D. Kingery, Physical Ceramics, Wiley, New York, 1997.
- [15] S. Stramare, V. Thangadurai, W. Weppner, Chem. Mater. 15 (2003) 3974.[16] M.F. Ashby, D.R.H. Jones, Engineering Materials: An Introduction to their Prop-
- erties and Applications, Pergamon Press, Oxford, 1980. [17] D.W. Richerson, Modern Ceramic Engineering: Properties, Processing and Use in Design, second ed., Marcel Dekker Inc., New York, 1992.
- [18] K.-Y. Yang, J.-W. Wang, K.-Z. Fung, J. Alloys Compd. 458 (2008) 415.
- [19] J. Jamnik, J. Maier, J. Electrochem. Soc. 146 (1999) 4183.
- [20] R.A. Huggins, Ionics 8 (2002) 300.
- [21] J.E. Baurle, J. Phys. Chem. Solids 30 (1969) 2657.
- [22] J. Fu, Solid State Ionics 96 (1997) 195.
- [23] D. Zhu, F. Luo, A. Xie, W. Zhou, Rare Met. 25 (2006) 39.
- [24] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G. Adachi, Chem. Lett. (1990) 331.
- [25] G. Adachi, N. Imanaka, H. Aono, Adv. Mater. 8 (1996) 127.
- [26] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G. Adachi, J. Electrochem. Soc. 140 (1993) 1827.
- [27] H. Aono, É. Sugimoto, Y. Sadaoka, N. Imanaka, G. Adachi, Solid State Ionics 47 (1991) 257.
- [28] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G. Adachi, J. Electrochem. Soc. 137 (1990) 1023.
- [29] A.V. Virkar, R.S. Gordon, J. Am. Ceram. Soc. 60 (1977) 58.
- [30] J.P. Singh, A.V. Virkar, D.K. Shetty, R.S. Gordon, J. Am. Ceram. Soc. 62 (1979) 179.
- [31] S.C. Carnigila, J. Am. Ceram. Soc. 48 (1965) 581.