传感器电解质 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ 的导电性能

包金小*, 王威威, 郭文荣

内蒙古科技大学材料与冶金学院, 包头 014010

* 联系人, E-mail: baojinxiao2004@yahoo.co.jp

2015-08-31 收稿, 2015-09-30 修回, 2015-10-23 接受, 2015-12-01 网络版发表

国家自然科学基金(51464038)、内蒙古自然科学基金(2014BS0507)和内蒙古科技大学孵化期项目(2014CY012/2012NCL023)资助

摘要 采用固相反应法在1673 K合成了 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ ($x=0, 0.005, 0.01, 0.02$)陶瓷粉体, 在空气中1873 K下对材料进行二次烧结10 h. X射线衍射物相分析结果确定合成后的样品中有 CaZrO_3 基固溶体和微量的 MgO 存在. 为了明确 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ 的电化学性能, 采用交流阻抗法在1073~1473 K, 富氧气氛($\text{Ar}/\text{O}_2/\text{D}_2\text{O}$)/($\text{Ar}/\text{O}_2/\text{H}_2\text{O}$)和富氢气氛($\text{Ar}/\text{H}_2/\text{H}_2\text{O}$)/($\text{Ar}/\text{D}_2/\text{D}_2\text{O}$)下测量了固体电解质的电导率及其同位素效应与气氛依赖性. 通过检测电导率的H/D同位素效应, 确定了固体电解质的质子导电优势区域. 结果显示在富氢气氛下, 测定的1073~1473 K温度范围内有明显的H/D同位素效应, 表明质子是主要的载流子. 在富氧气氛下, 1073~1273 K温度范围内, 质子也是主要的载流子. 该材料有可能作为氢传感器的固体电解质.

关键词 稀土, 质子, 电导率, 同位素效应, 质子导体

目前, 离子器件和电子器件一样得到了巨大的发展, 尤其是在熔融金属等冶炼领域得到了广泛的应用, 例如金属液定氢传感器. 铜和铜合金具有良好的综合性能, 在国民经济和国防中有一系列的重要用途, 而冶炼过程中, 当熔铜和铜合金凝固时, 氢的析出会使铸件和板材中形成气孔、白点等缺陷, 显著降低产品的气密性、强度、塑性、冲击韧性及断裂韧性, 进而对薄板材料、动力车及航空部件的性能产生严重影响, 因此有必要对铜液中的氢含量进行监测及控制. 目前, 固体电解质, 尤其是缺陷结构型质子导电氧化物材料已经被广泛应用于铝合金熔体中氢气浓度的测量. 随着固体电解质理论及应用的不断发展^[1-5], 开发具有更高测量精度、更长工作时间、更低廉价格且适用于工业环境的铜液定氢电化学传感器、进而促进冶金和材料生产的发展已经成为研究机构以及工厂的研究热点. 对金属熔液中的氢含量进行准确、简便的测量在冶金及材料生产过程中具有

十分重要的意义, 但现有的氢传感器存在着连续工作时间短、测量精度差和价格昂贵等一系列问题, 研究较为广泛的氢传感器电解质(In掺杂 CaZrO_3)在低温领域有较好的化学稳定性, 且在铝液定氢传感器中获得了应用, 但在1473 K以上温度下化学稳定性差, 影响掺杂效果^[6-13], 导致金属液定氢传感器的测量精度不高^[14-17], 限制了其在工业环境中的应用. 为此本文开展了对 CaZrO_3 掺杂Mg的研究, 制备了不同掺杂量的样品, 并采用交流阻抗谱法测定其不同温度下的电导率; 分析了质子导电优势区域, 电导率与掺杂量的关系, 由实验总结出电导率与掺杂量及温度的相关关系, 得到该材料的最佳掺杂量, 为该材料的进一步扩大应用奠定基础. 本文在阐明其质子电导优势区域及化学稳定性的基础上探讨其在金属熔融传感器电解质上应用的可能性. 此类质子导体材料比氧化锆系列制作成本较低, 具有重要的应用价值.

引用格式: 包金小, 王威威, 郭文荣. 传感器电解质 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ 的导电性能. 科学通报, 2016, 61: 791-796

Bao J X, Wang W W, Guo W R. Properties of electric conductivity of $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ in sensors electrolyte (in Chinese). Chin Sci Bull, 2016, 61: 791-796, doi: 10.1360/N972015-00994

1 实验

(i) 固体电解质制备. 制备试样的出发原料为 CaCO_3 (分析纯)、 ZrO_2 (分析纯)和 MgO (分析纯), 按目标产物 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ ($x=0, 0.001, 0.005, 0.02$)的化学计量比称量原料, 采用固相合成法制备质子导体固体电解质. 以无水乙醇为介质, 置于砂磨机中砂磨2 h, 转速为2500 r/min. 将混合、砂磨、干燥后的粉体在10 MPa 压力下用小型双向液压机进行压片. 成型的试样在空气气氛下1673 K恒温煅烧10 h, 将煅烧后的样品, 用砂磨机研磨2 h, 得到自制粉体, 采用Verneuil法制备试样. 使用冷等静压在200 MPa的压力下将合成后的粉料压制成型后, 在空气中1873 K下烧结16 h进行二次烧结, 提高了样品的强度及致密度. 采用Philips PW 3040/60型X射线衍射仪(XRD, $\text{Cu K}\alpha$, 单晶硅做内标)对煅烧后的粉料进行XRD物相分析, 确认合成了 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ 粉体. 得到的样品为直径6.3 mm, 厚度0.72 mm的圆片. 在本文中, 采用致密度96%或更高的样品进行电导率及H/D同位素测试.

(ii) 样品测试. 在固相合成制备的试样 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ ($x=0, 0.001, 0.005, 0.02$)的2个面上涂1层铂浆, 1073 K下煅烧4 h, 连接铂金丝及铂金电极组成电池. 氛围气体是 $(\text{Ar}/\text{O}_2/\text{D}_2\text{O})/(\text{Ar}/\text{O}_2/\text{H}_2\text{O})$, $(\text{Ar}/\text{H}_2/\text{H}_2\text{O})/(\text{Ar}/\text{D}_2/\text{D}_2\text{O})$, 混气装置控制炉内气氛(恒温带长度大于80 mm, 精度为 ± 1 K), 把混合好的气体通过水蒸气饱和装置保持一定的水分压. 电化学测量采用NF制造的2345LCZ阻抗仪(测量频率: 40~100 Hz)和HIOKI制造的3532-80化学阻抗仪(测量频率: 4 Hz~1 MHz, 电化学接口3532-80), 试样的质子导体电导率及H/D同位素效应在1073~1673 K, 40~100 kHz频率范围下进行测量, 实验装置如图1所示.

2 结果与分析

2.1 XRD物相分析

出发原料 CaCO_3 , ZrO_2 和 MgO 混合, 经1673 K恒温10 h 煅烧后得到的 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ ($x=0, 0.005, 0.10, 0.15$)粉体的XRD图谱如图2所示. 煅烧粉体的衍射峰位置和相对强度与 CaZrO_3 标准峰基本一致, 且未检测到原始氧化物, 说明混合粉料经1673 K恒温10 h 煅烧已经形成预期的钙钛矿型 CaZrO_3 基固溶体. 掺杂后的主峰相对于标准峰发生微弱偏移, 这是

图1 电导率测试装置

Figure 1 Schematic view of experimental apparatus

由于 Mg^{2+} 的半径为0.078 nm, Zr^{4+} 的半径为0.072 nm, 较大离子半径的 Mg^{2+} 掺杂替代 Zr^{4+} 产生晶格畸变, 致使衍射峰位置发生微小偏移. 而当掺杂量 $x=0.01$ 以上时, 样品的XRD图谱中出现了微量第二相 MgO . 因此, Mg 掺杂 CaZrO_3 的固溶极限为0.1 %(摩尔百分比).

2.2 H/D同位素效应

根据同位素效应原理, 当电解质中优势的电荷载体为质子的情况下H/D电导率相差1.37倍, 是由于电荷载体从质子置换成重氢时质量变化而导致. 如图3所示, 在923 K下, 对 $\text{CaZr}_{0.995}\text{Mg}_{0.005}\text{O}_{3-\alpha}$ 固体电解质进行了同位素测量. 当测试环境气氛由 $(\text{Ar}/\text{D}_2/\text{D}_2\text{O})$ 变为 $(\text{Ar}/\text{H}_2/\text{H}_2\text{O})$ 时, 电解质的阻抗变小, 达到

图2 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ 的XRD图谱

Figure 2 XRD pattern for $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$

图3 $\text{CaZr}_{0.995}\text{Mg}_{0.005}\text{O}_{3-\alpha}$ 的H/D同位素效应测试结果
Figure 3 H/D isotope effect on the electrical conductivity for $\text{CaZr}_{0.995}\text{Mg}_{0.005}\text{O}_{3-\alpha}$

平衡以后的电导率相差1.33倍,这与Al掺杂 CaZrO_3 系统检测到的结果相似^[6]. H/D同位素效应检测结果表明,923 K的低温区域,质子是优势电荷载体.综合电导率H/D同位素分析结果,制备的固体电解质在973 K左右的温度区域优势的电荷载体是质子.这初步确定 $\text{CaZr}_{0.995}\text{Mg}_{0.005}\text{O}_{3-\alpha}$ 具有质子导电性,关于更高温度区域的质子电导特性在温度与电导率测试结果中进行讨论.

2.3 电导率对温度的依赖性

在一般的固体电解质质子导体的质子传输原理中,试样的电阻分为晶粒阻抗、晶界阻抗及两面烧结的测量电极阻抗.样品的电阻 R 可以根据交流阻抗谱得出,在不同温度下试样的电导率可以利用式(1)进行计算.式中 σ 是样品电导率(S/cm), R 是试样电阻(Ω), L 为试样厚度(cm), S 是试样截面积(cm^2).

$$\sigma = L/RS. \quad (1)$$

在含水氙气气氛中,不同温度下分别测定了 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ ($x=0.001, 0.015, 0.02$)的交流阻抗谱,结果示于图4, R 和 $-X$ 分别指实部与虚部.结果表明,随着温度的升高, $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ 的阻抗逐渐减小,因为随着环境温度的升高在固体电解质中的质子迁移速度加快.

在不同气氛下($\text{Ar/O}_2/\text{D}_2\text{O}$)/($\text{Ar/O}_2/\text{H}_2\text{O}$), ($\text{Ar/H}_2/\text{H}_2\text{O}$)/($\text{Ar/D}_2/\text{D}_2\text{O}$)得到不同掺杂量 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ 的电导率与温度的关系图,如图5所示.根据不同温度下的实验数据及式(1)的计算结果,用 $\ln(\sigma T)$ 对 $1000/T$ 进行绘图,结果显示 $\ln(\sigma T)-1000/T$ 呈近似线性关系,此结果符合Arrhenius公式(式(2)).式中, E_a 为电导激

图4 $\text{CaZr}_{0.995}\text{Mg}_{0.005}\text{O}_{3-\alpha}$ 不同温度下的电阻变化
Figure 4 Resistance change of $\text{CaZr}_{0.995}\text{Mg}_{0.005}\text{O}_{3-\alpha}$ under different temperatures

活能(eV),常数 A 与电解质本性、结构等有关, k 为Boltzman常数, T 表示温度(K).

$$\ln(\sigma T) = \ln A - E_a/kT. \quad (2)$$

根据Arrhenius公式及实验结果,不同温度及不同掺杂量时 $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ 的电导率与温度的Arrhenius曲线结果如图5所示.在富氧气氛中,低温(1473 K或更低)时有H/D同位素效应,因此,在这些条件下,质子似乎成为主要的载流子.相反,在高温(1473 K或更高)没有H/D同位素效应,所以在更高的温度区内主要载流子不是质子.另一方面,在富氢气氛下,几乎整个测量温度范围内均有H/D同位素效应,因此,在这些条件下,质子导电似乎是主要的导电种类.电导率的这些气氛依赖性与Al掺杂 CaZrO_3 系统检测到的结果相似.在2种气氛中, $\text{CaZr}_{0.99}\text{Mg}_{0.01}\text{O}_{3-\alpha}$ 的电导率均比 $\text{CaZr}_{0.99}\text{Mg}_{0.01}\text{O}_{3-\alpha}$ 的高^[7,8].受主掺杂的增加通常会导致载流子如孔穴、质子和氧离子空位的浓度的升高.因此,这种增加趋势是合理的.在2种气氛中, $\text{CaZr}_{0.99}\text{Mg}_{0.01}\text{O}_{3-\alpha}$ 受主掺杂 X 的增加通常会导致载流子如孔穴、质子和氧离子空位的浓度的升高.实验结果表明, M 掺杂量对氧化铝基陶瓷质子导电性能有明显的影响,但掺杂量并非越多越好:(1)过多的氧缺陷,往往会发生质子捕获形成稳定的结构,对质子传输不利;(2)过多的掺杂导致生成第二相,阻碍质子的迁移速度.因此,严格控制 M 掺杂量的基础上可以获得高电导率及质子迁移率的固体质

图5 氢气(a)和氧气(b)气氛下电导率随掺杂量及温度变化的Arrhenius曲线

Figure 5 Arrhenius plots of the electrical conductivity under hydrogen (a) and oxygen-rich (b) atmospheric conditions

子导电材料。

2.4 电导率的气氛依赖性

固体电解质质子导体材料的导电率与外围气氛的关联,使用电化学工作站测量,阐明了稀土离子掺杂量、温度、气体分压、气体流速、气氛对固体电解质质子导电率的影响。固体电解质的质子导电性(σ_{H^+})与质子电荷数(e)、质子浓度(C_{H^+})、质子迁移率(μ_{H^+})、质子扩散率(D_{H^+})及与其邻近的晶格氧离子的结合能有关。通过实验和模拟可以揭示影响质子传输的各种因素之间的关系。关于锆酸钙质子导体的质子导电机理虽有许多探索与研究,但并未形成一种成熟的理论。导电机理方面的研究可以用缺陷理论来解释,由于低价元素M的掺杂,占据Al位后产

生负电荷,根据电中性原理,同时必然产生带正电荷的氧空位或者电子空穴,从而在含氢或水蒸气气氛中产生质子。

当 H_2O 活度为0.01时,在富氧气氛下测得的电导率作为氧活度的函数log-log图如图6(a)所示。从图中可以看出,在较高温度下,电导率成比例增加至近似氧活度的1/4。在低的温度范围,电导率与氧活度的关系趋势不再明显。根据电导率与温度依赖结果可测得的H/D同位素效应,质子是主要载流子。当氧活度设定在0.01时,电导率与水蒸气关系的函数log-log图如图6(b)所示。从图中可以看出,在较高温度下,电导率保持恒定,与水蒸气活度无关,反之在较低温度范围内,即质子成为主要的载流子,电导率呈现出成比例增长,达到蒸气活度的1/2。

图6 富氧气氛下的电导率与环境气氛的关系。(a) 氧气;(b) 水蒸气

Figure 6 The oxygen (a) and water vapor (b) activity dependence of electrical conductivity in an oxygen-rich atmosphere

3 结论

根据粉末衍射实验结果, Mg掺杂CaZrO₃中Mg的固溶极限为0.2 mol. CaZr_{1-x}Mg_xO_{3-α}同位素效应及电导率的测量结果显示, 在1073~1473 K温度范围内、富氧气氛下, 质子是主要的载流子. 电导率随着

温度的升高而增大, 且随着水蒸气分压的增大呈现逐渐增大的趋势.

这些结果表明, CaZrO₃中掺杂Mg质子导体固体电解质在富氢气氛下, 有较纯的质子电导率, 是一种替换现在使用的金属液氢传感器探针In掺杂CaZrO₃的备选材料.

参考文献

- 1 Medvedev D, Lyagaeva J, Plaksin S, et al. Sulfur and carbon tolerance of BaCeO₃-BaZrO₃ proton-conducting materials. *J Power Sources*, 2015, 273: 716–723
- 2 Zhao R R, Hung I M, Li Y T, et al. Synthesis and properties of Co-doped LiFePO₄ as cathode material via a hydrothermal route for lithium-ionbatteries. *J Alloy Compd*, 2012, 513: 282–288
- 3 Chen J H, Shen M Q, Wang X Q, et al. Catalytic performance of NO oxidation over LaMeO₃ (Me = Mn, Fe, Co) perovskite prepared by the sol-gel method. *Catal Commun*, 2013, 37: 105–108
- 4 Wang S W, Zhao F, Zhang L L, et al. Stability and electrical property of Ba_{1-x}Sr_xCe_{0.8}Y_{0.2}O_{3-δ} high temperature proton conductor. *J Alloy Compd*, 2010, 506: 263–267
- 5 Yuan W, Xiao C, Li L. Hydrogen permeationand chemical stability of In-doped SrCe_{0.95}Tm_{0.05}O_{3-δ} membranes. *J Alloy Compd*, 2014, 616: 142–147
- 6 Waser R. Diffusion of hydrogen defects in BaTiO₃ ceramics and SrTiO₃ single crystals. *Bunsenges B Phys Chem*, 1986, 90: 1223
- 7 Kreuer K D. On the development of proton conducting materials for technological applications. *Solid State Ion*, 1997, 97: 1–15
- 8 Müller J, Kreuer K D, Maier J, et al. A conductivity and thermal gravimetric analysis of a Y-doped SrZrO₃ single crystal. *Solid State Ion*, 1997, 97: 421–427
- 9 Scholten M J, Schoonman J, van Miltenburg J C. Synthesis of strontium and barium cerate and their reaction with carbon dioxide. *Solid State Ion*, 1993, 61: 83–91
- 10 Yajima T, Kazeoka H, Yogo T. Proton conduction in sintered oxides based on CaZrO₃. *Solid State Ion*, 1991, 47: 271–275
- 11 Cano C, Osendi M I, Belmonte M, et al. Effect of the type of flame on the microstructure of CaZrO₃ combustion flame sprayed coatings. *Surface Coat Technol*, 2006, 201: 3307–3313
- 12 Shimura T, Esaka K, Matsumoto H. Protonic conduction in Rh-doped AZrO₃ (A=Ba, Sr and Ca). *Solid State Ion*, 2012, 149: 237–246
- 13 Zheng W, Pang W, Meng G. Hydrothermal synthesis of SrZrO_{3-α} (M=Al, Ga, In, $x \leq 0.20$) series oxides. *Solid State Ion*, 1998, 108: 37–41
- 14 Bao J, Ohno H, Kurita N, et al. Proton conduction in Al-doped CaZrO₃. *Electrochim Acta*, 2011, 56: 1062–1068
- 15 Le J, van Rij L N, van Landschoot R C, et al. A wet-chemical method for the synthesis of In-doped CaZrO₃ ceramic powders. *J Eur Ceram Soc*, 1999, 19: 2589–2591
- 16 Han J D, Wen Z Y, Zhang J C, et al. Synthesis and characterization of proton conductive CaZr_{0.90}In_{0.10}O_{3-δ} by a citric acid complexation method. *Fusion Eng Des*, 2010, 85: 2100–2104
- 17 Ahmed I, Eriksson S G, Ahlberg E, et al. Synthesis and structural characterization of perovskite type proton conducting BaZr_{1-x}In_xO_{3-δ} (0.0≤x≤0.75). *Solid State Ion*, 2015, 177: 1395–1403

Properties of electric conductivity of $\text{CaZr}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$ in sensors electrolyte

BAO JinXiao, WANG WeiWei & GUO WenRong

School of Material and Metallurgy, Inner Mongolia University of Science and Technology, Baotou 014010, China

For measurement of high-temperature combustion gases such as NO_x , CO , H_2 , etc., mixed potential gas sensors utilized solid-electrolyte yttria-stabilized zirconia (YSZ) and metal-oxide sensing electrodes have been known as very good and promising selections. One of the most interesting sensing electrodes material is the perovskite-type oxide ABO_3 (A cation of rare earth element, B cation of 3d transition metal and O anion of oxygen) due to having more exciting gas-catalytic characteristics, stability and robustness in high temperature environments. Proton or oxide-ion conducting solid oxide electrolytes are useful for various electrochemical devices. They have been also proposed for membrane reactors, e.g., in particular, solid oxide fuel cells (SOFCs) are important as alternative electrical power generating systems with high energy-conversion efficiency. Recently, several perovskite-type proton conducting oxides, such as CaZrO_3 and BaCeO_3 based materials, have been suggested as alternate electrolyte materials for the intermediate temperature fuel cells owing to their higher ionic conductivities and lower the activation energy as compared to the conventional oxygen-ion conducting electrolytes. In this class of compounds, yttrium-doped CaZrO_3 (CZY) and BaCeO_3 (BCY) have exhibited considerable proton conductivity with low migration energy in the intermediate temperature range. Nevertheless, materials for proton conducting membranes are still not sufficiently developed, and therefore extensive investigations of proton absorption and migration mechanisms, as well as further application tests are needed. As a solid electrolyte has the properties of both solid and ion conductor, it has been generally utilized conveniently for chemical sensors, fuel cells, coulometric measurement devices, etc.

In this study, $\text{CaZrO}_{3-\alpha}$ based solid electrolyte was prepared by a solid-state reaction method, starting materials are the 99.99% purity CaCO_3 , ZrO_2 and MgO powders. The mechanochemical treatment was carried out in a nitrogen atmosphere using a planetary ball mill with an agate pot and ball. The rotation speeds of the milling pot and table were maintained at 720 r/min with a constant rotation ratio of 1:1:1 for 1 h. The volume of the pot was 45 mL and 10 balls of 10 mm diameter were used for the mechanochemical treatment. The powders were mixed in a ball mill and cold-isostatically pressed into pellets at 200 MPa, and finally sintered at 1600 °C for 10 h in air. The pellets were ground again and sieved into a uniform-sized powder. The powder was pressed into pellets using 10-mm diameter dies at a pressure of approximately 1.5 ton/cm², and then statically pressed at a pressure of approximately 2 ton/cm². Finally, the pellets were calcined in alumina crucibles at the optimum temperature 1873 K for 16 h in air to obtain $\text{CaZrO}_{3-\alpha}$ based solid electrolyte polycrystalline ceramics. To clarify the high temperature electrochemical properties of Mg-doped CaZrO_3 , the electrical conductivity of the poly-crystalline specimen was measured in various kinds of hydrogen and oxygen-containing atmospheres by employing the two terminal AC method. The H/D isotope effect of the electrical conductivity was examined in detail in order to specify the conditions in which the proton conduction was dominant. In the temperature range from 1073 to 1473 K, it was found that protons were the dominant charge carrier both in hydrogen-rich and oxygen-rich atmospheres. The material is likely to serve as a solid electrolyte for hydrogen sensor.

rare earth, proton, conductivity, isotope effect, hydrogen sensor

doi: 10.1360/N972015-00994