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湿化学法制备的
 $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\text{-La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_3$ 复
合阴极研究

Study of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\text{-La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_3$ Composite
Cathodes Synthesized by Using the Wet Chemistry Method

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**Study of $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ -
 $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_3$ Composite
Cathodes Synthesized by Using the Wet
Chemistry Method**



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By

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摘要

$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ 是一种较好的 ITSOFC 阴极材料, 负载于镓酸镧电解质上的 $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 - \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_3$ (SSC-LSGMC5) 复合阴极表现出高的活性与稳定性。SSC-LSGMC5 复合阴极制备方法的探索及氧还原机理的研究对于开发高性能阴极材料具有重要意义。本文采用湿化学法制备了 SSC-LSGMC5 复合阴极, 利用多种电化学技术对电极上的氧还原反应动力学进行了研究。

首次用湿化学法制备了 SSC-LSGMC5 复合电极。SSC-LSGMC5 复合阴极中的 SSC 及 LSGMC5 粉分别采用甘氨酸-硝酸盐法和柠檬酸盐法合成。相对于固相合成法, 湿化学法有效地降低了 SSC 及 LSGMC5 的成相温度。利用湿化学法合成的 SSC、LSGMC5 粉末制备出的 SSC-LSGMC5 复合电极的性能, 显著高于固相合成法制备的电极。其高性能与电极体相及电极/电解质界面微观结构的改善有关。电极的性能显著依赖于 SSC、LSGMC5 粉末的焙烧温度, SSC 及 LSGMC5 粉末的最佳焙烧温度分别在 1223 和 1273 K 附近。优化了负载在 LSGM 电解质片上的 SSC-LSGMC5 复合电极的焙烧温度, 1223 K 焙烧的电极具有最小的欧姆电阻及电极极化电阻。

考察了 SSC-LSGMC5 中 LSGMC5 粉末含量对电极性能及氧还原反应的影响。LSGMC5 的掺入显著减小了电池的欧姆电阻。高温下 SSC-LSGMC5 (15 wt.%) 的电极活性明显高于纯 SSC 电极, LSGMC5 掺入量的进一步增加导致电极活性降低。

电化学测试结果表明, 负载于 LSGM 电解质上的 SSC-LSGMC5 (0-30 wt%) 电极在高温、低氧分压下的阻抗谱中通常包括三个阻抗半圆。高频环较小并且与氧分压及极化电位无关。该环随电极中 LSGMC5 掺入量的增大而减小, 可能对应于氧离子在电极/电解质界面的传递过程。中频环的氧分压级数通常为 1/4, 对应于电荷转移步骤。低频环氧分压级数为 1, 对应于氧气分子扩散过程。低温、高氧分压下低频环消失, 氧还原反应主要由电荷转移过程控制。负载于 LSGMC5 电解质上的 SSC-LSGMC5 (15 wt.%) 的氧还原反应机理与负载于 LSGM 电解质上的相近, 但阻抗谱中未出现明显的高频环。

关键词: $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ 阴极, 湿化学法, 氧还原

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SSC-LSGMC5 composite cathodes were prepared by using the wet-chemistry method for the first time. The SSC and LSGMC5 powders in the SSC-LSGMC5 cathodes were synthesized by using the glycine-nitrate method and citrate method, respectively. Compared with the solid-state reaction, the SSC and LSGMC5 powders synthesized using by the wet-chemistry method can form ideal phases at a lower temperature. SSC-LSGMC5 cathodes consisted of SSC and LSGMC5 powders synthesized by using the wet-chemistry method exhibited higher performance than that synthesized by using the solid-state reaction, and the high performance of the electrodes could be related to the improvement in the microstructure of electrode bulk and electrode/electrolyte interface. The performance of the electrodes depended strongly on the sintering temperature of SSC and LSGMC5, and the optimum sintering temperatures for SSC and LSGMC5 were about 1223 and 1273 K, respectively. The sintering temperature of SSC-LSGMC5 supported on LSGM was optimized. The electrode sintered at 1223 K exhibited the lowest ohmic resistance and polarization resistance.

Effect of the concentration of LSGMC5 in SSC-LSGMC5 electrode on the oxygen reduction reaction was studied. The introduction of LSGMC5 into SSC decreased the ohmic resistance of the cell. The electrode activity of SSC-LSGMC5(15 wt.%) was higher than that of pure SSC electrode at high temperatures. With the further increase in the amount of LSGMC5 in the electrode, the electrode activity

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The results of electrochemical measurements showed that the impedance spectra of SSC-LSGMC5 (0-30 wt%) supported on LSGM were consisted of three impedance arcs at high temperatures and low oxygen partial pressures. The arc at high frequency was small and independent on the oxygen partial pressure and polarization potential. The arc decreased with the increase in the amount of LSGMC5 in the SSC-LSGMC5 electrode, which could correspond to the transfer of oxygen ions across the electrode/electrolyte interface. The arc at intermediate frequency showed a oxygen partial pressure dependency about 1/4, corresponding to the charge transfer process. The oxygen partial pressure dependency of the low frequency arc was about 1, which was related to the gas diffusion of oxygen molecule. The arc at low frequency disappeared at low temperatures and high oxygen partial pressures, and the oxygen reduction reaction was controlled by the charge transfer process. The oxygen reduction mechanism of SSC-LSGMC5 (15 wt.%) supported on LSGMC5 was similar to that supported on LSGM. However, the arc at high frequency did not appear in the impedance spectra.

Keywords: $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cathode; the wet-chemistry method; oxygen reduction

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Keywords: $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cathode; the wet-chemistry method; oxygen reduction

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厦门大学博硕士论文摘要库

第一章 前言

1.1 燃料电池概述

燃料电池(Fuel Cell)是一种将储存在燃料与氧化剂中的化学能直接转化为电能的发电装置^[1-2]。这种装置的最大特点是由于反应过程中不涉及到燃烧,因此其能量转换效率不受“卡诺循环”的限制,其能量转换效率高达 50—80%,实际使用效率则是普通内燃机的 2—3 倍。另外,它还具有燃料多样化、环境污染小、可靠性及维修性好等优点^[3-6]。

早在内燃机问世之前(1842 年),英国的 William Grove 就展示了世界上第一台以稀硫酸为电解质, H₂ 为燃料, O₂ 为氧化剂的电化学能量转化装置。而到本世纪 50 年代之前,由于电池材料的限制、电极过程动力学理论的落后以及在 19 世纪后期内燃机这种相对简单的能量转化装置的问世和迅速发展,燃料电池的发展一直处于停滞状态^[7-8]。本世纪中叶,在宇航工业发展的推动下,常温氢氧燃料电池技术有了长足的发展。但当时该类燃料电池系统造价昂贵,只能在航天、军事等特殊场合应用。近年来,由于矿物资源的日趋贫乏和保护生态环境日益受到重视,人们迫切希望发展高效的既可节省有限矿物资源、又可减少污染物排放的环境友好发电技术。燃料电池发电技术正好满足以上要求,重新受到人们的重视。燃料电池从第一代碱性燃料电池(AFC)开始,已经发展到第五代质子膜燃料电池(PEMFC)。除 AFC 电池外,第二代磷酸电池(PAFC)、第三代熔融碳酸盐(MCFC)、第四代固体氧化物燃料电池(SOFC)和第五代质子膜燃料电池(PEMFC),各有其某方面的优点,目前正向商业化发展^[8-9]。

1.2 固体氧化物燃料电池的特点及工作原理

1.2.1 特点

固体氧化物燃料电池(Solid Oxide Fuel Cells, SOFC),又称陶瓷膜燃料电池(Ceramic Membrane Fuel Cells)是 20 世纪 80 年代迅速发展起来的第四代燃料电池。SOFC 系统是一种直接将燃料气体和氧化物中的化学能转换成电能的全固体能量转换装置。与其他燃料电池不同,在 SOFC 中,采用固体氧化物氧离子导体

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