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锂氧电池钙钛矿型 $LaFeO_3$ 阴极电催化剂的制备、表征和性能研究

Preparation, characterization and properties of $LaFeO_3$ perovskite electrocatalysts for lithium-oxygen battery

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Preparation, characterization and properties of $LaFeO_3$ perovskite electrocatalysts for lithium-oxygen battery

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摘 要

高能量密度的锂氧电池是极具应用价值的下一代储能装置。目前，它的研究仍处于基础探索阶段。面临的关键问题包括氧气电极缓慢的反应动力学，放电过程中 Li_2O_2 等导电性较差的放电产物在电池氧气阴极沉积，导致锂氧电池的电化学极化过大、循环性能不稳定和倍率性能受限等。解决方法之一是构建高效的阴极电催化剂：一方面提高电催化剂的氧还原（ORR）和氧释放（OER）催化反应动力学；另一方面通过优化的结构设计促进电子传输、氧气扩散、电解液浸润和放电产物存储。

本文选择钙钛矿型化合物 $LaFeO_3$ 为主要研究对象。首先制备了 $LaFeO_3$ 纳米粒子(NP-$LaFeO_3$)，通过电化学方法研究了该电催化剂的本征催化活性；随后，针对 $LaFeO_3$ 体相导电性差，本征催化活性较弱的问题，对其复合改性。制备出石墨烯-铁酸镧（RGO-$LaFeO_3$）和 RuO_2/$LaFeO_3$（RuO_2/BLF）复合纳米电催化剂。运用 XRD、SEM、FTIR、N_2 等温吸脱附等表征分析材料的结构和形貌，通过电化学测试和对放电产物的形貌结构表征，分析所制备的电催化剂的催化活性及催化机理，并组装到锂氧电池中表征了电池的性能。主要研究结果如下：

（1）采用 Pechini 法，通过优化反应溶液 pH（最佳 pH 值为 9）、煅烧温度（最佳煅烧温度 900 ℃）和煅烧方式（最佳直接高温煅烧方式）等制备条件，得到部分类球形颗粒相连接的短棒状 NP-$LaFeO_3$ 电催化剂。以电催化剂作为阴极的锂氧电池，在限定 500 $mAh·g^{-1}$ 放电比容量的条件下，电池可稳定循环 40 周，并展现出优于乙炔黑锂氧电池的能量效率和循环稳定性。

（2）发展了一种原位制备 RGO-$LaFeO_3$ 复合纳米电催化剂的方法。电化学测试表明：引入 RGO 后，电催化剂的 ORR 和 OER 催化活性均得到明显提升，RGO-$LaFeO_3$ 作为阴极电催化剂的锂氧电池，限定 500 $mAh·g^{-1}$ 比容量、在 100 $mA·g^{-1}$ 电流密度条件下进行充放电，电池可稳定循环 70 周。对充放电到不同阶段的氧气电极进行的 SEM 和 XRD 分析均可推测到 Li_2O_2 的形成和分解。这种优异的电化学性能主要归结于：一方面 RGO 与 $LaFeO_3$ 纳米粒子间具有协同催化作用，另一方面 RGO-$LaFeO_3$ 电催化剂兼具介孔与大孔的三维导电多级孔结构。

（3）结合水热法和浸渍法，在带有大量介孔的 $LaFeO_3$ 微球（BLF）表面负

载 RuO_2 纳米粒子。电化学测试结果表明：引入 RuO_2 后，RuO_2/BLF 复合纳米电催化剂的 OER 活性明显加强；RuO_2/BLF 作为阴极电催化剂的锂氧电池，在限定 500 $mAh \cdot g^{-1}$ 比容量、100 $mA \cdot g^{-1}$ 电流密度条件下进行充放电，电池可稳定循环 65 周，充放电过电位为 0.90 V。通过对充放电过程前后氧气电极的 SEM 和 XRD 表征，结果表明放电产物为 300 nm 左右小尺寸的 Li_2O_2，RuO_2/BLF 可诱导 Li_2O_2 存储于 $LaFeO_3$ 微球表面的介孔和 $LaFeO_3$ 纳米粒子间隙中，使得电催化剂的反应位点得以保留，从而促进 Li_2O_2 在充电过程中高效分解。

本论文的研究工作拓展了锂氧电池钙钛矿型阴极电催化剂的应用，在催化剂设计和合成方法方面具有一定的创新性，为构建 ORR 和 OER 双效电催化剂提供了新思路。

关键词： 锂氧电池；双效催化；$LaFeO_3$；石墨烯；RuO_2

Abstract

Non-aqueous lithium-oxygen battery is a promising candidate for next generation energy storage due to its high specific capacity. Now its research still stay at fundamental exploration, and one of the most important problems is focused on the sluggish oxygen reaction kinetics. During the discharge process, masses of isolated products which are mainly consisted of lithium peroxide deposit on oxygen electrode, hindering the electronic transfer, leading to large polarization and limiting the capacity and cycle stability of the Li-O_2 battery. Designing high efficient bifunctional electrocatalysts is considered to be one of the most effective strategies, including the optimized design of cathode structures and the enhancement of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) kinetics.

In this paper, $LaFeO_3$ was chosen as the main research object, and in order to investigate $LaFeO_3$'s inherent catalytic activity, $LaFeO_3$ nanoparticles (NP-$LaFeO_3$) were firstly prepared, and their electrocatalytic activity were characterized via electrochemical technology. Subsequently, in view of poor conductivity and slightly weak catalytic activity of the $LaFeO_3$, compound modification method was taken to further optimize its electrocatalytic activity. Based on this strategy, reduced graphene oxide-$LaFeO_3$ (RGO-$LaFeO_3$) and RuO_2/$LaFeO_3$ nanocomposite electrocatalysts were explored in lithium-oxygen battery, their morphologies and structures were observed by characterization technologies such as XRD, SEM, FTIR, N_2 sorption isotherms, etc. Besides, electrochemical test and discharge product characterization results were combined to analysis mechanism of catalytic reaction. Meanwhile, all elecrtocatalysts were applied in Li-O_2 batteries to test the battery performances. The main research achievements were obtained as follows:

(1) NP-$LaFeO_3$ was prepared via Pechini method, and three vital experiment factors were studied in detail. When pH value of reaction solution was 9, calcination temperature was 900 ℃ and the precursor was calcined directly at high temperature without grinding before, $LaFeO_3$ nanoparticles with rod morphology composed of some sphere-like particles were successfully abtained. The Li-O_2 battery with NP-$LaFeO_3$ electrocatalyst sustained 40 cycles at 500 $mAh \cdot g^{-1}$, and showed better electrical energy efficiency than acetylene black catalyzed battery.

(2) A new synthesis method was developed to get RGO-$LaFeO_3$ nanocomposite

electrocatalyst in situ. Chronoamperometry and linear sweep voltammetry test results demonstrated that RGO-$LaFeO_3$ exhibited enhanced ORR and OER activity compared with RGO and NP-$LaFeO_3$ electrocatalysts. Li-O_2 battery with RGO-$LaFeO_3$ electrocatalyst could maintain 70 reversible cycles with a limited capacity of 500 $mAh \cdot g^{-1}$ at a rate of 100 $mA \cdot g^{-1}$. Meanwhile, the formation and decomposition of Li_2O_2 at the specific discharge or charge state was characterized via the SEM and XRD tests of the oxygen electrode. These excellent performances are mainly attributed to two aspects: on one side RGO-$LaFeO_3$ nanocomposite electrocatalyst shows synergistic effect between RGO and $LaFeO_3$ nanoparticles, on the other hand the electrocatalyst possesses three-dimensional conductive heterogeneous structure with both meso and macro pores, which is good for discharge product storage, electronic transfer and oxygen diffusion.

(3) BLF micro-sphere decorated RuO_2 nanoparticles were synthesized by a combined method of hydrothermal reaction and impregnation. Chronoamperometry and linear sweep voltammetry tests were conducted to study its electrochemical property, After the decoration of the RuO_2 nanoparticles, the OER activity of the RuO_2/BLF was obviously enhanced. Meanwhile, the Li-O_2 battery with RuO_2/BLF was operated with 500 $mAh \cdot g^{-1}$ capacity at a current density of 100 $mA \cdot g^{-1}$, it could maintain 65 stable cycles and deliver a charge-discharge overpotential of 0.90 V. SEM and XRD characterization of the oxygen electrode demonstrated that RuO_2/BLF electrocatalyst could facilitate the formation of the Li_2O_2 with small size during the discharge process, and Li_2O_2 mainly stored in the mesopores on the surface of $LaFeO_3$ sphere or in the pile pores between $LaFeO_3$ nanoparticles, so that catalytic active sites could be retained to facilitate the decomposition of Li_2O_2 during the charge process.

The research work of this paper extended the application of perovskite type electrocatalyst for lithium-oxygen battery, and privided new strategies for constructing ORR and OER bifunctional electrocatalyst.

Keywords: Lithium-O_2 battery; Bifunctional electrocatalyst; $LaFeO_3$; Reduced graphene oxide; RuO_2

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