過渡金屬氧化物觸媒應用於鋅－空氣燃料電池陰極之研究

學生：黃雅君　　指導教授：林鵬

國立交通大學 材料科學與工程研究所

摘要

金屬－空氣燃料電池包括鋅－空氣及鋁－空氣電池，由於結構簡單、高比能量、原料便宜、性質安定以及諸多優點，此類電池已被應用在低功率的攜帶式電子設備上。為了符合國內未來在電動車輛上的能源需求，空氣陰極的活性(或是氧氣的還原速率)必須提升以達到高比能量/功率的規格。氧氣於鹼性電解液中的還原機制是在空氣陰極內部的導電粉體(如：碳黑加觸媒)表面上進行的，此粉體表面吸附反應物(O_2、H_2O及OH^-)與釋出生成物(OH^-及HO_2^-)等，其功能類似一個反應載體。其中觸媒對氧氣的還原催化性能是陰極活性的主要決定因素，考量廉價的觸媒才能以合理的成本進行量產實用化。

本研究著重於非貴重金屬的氧化物觸媒，以ACP法製備一系列過渡金屬氧化物，如：La-Ca-Co-O、Y-Ba-Cu-O、Ba-Ru-O、Co-O、Cu-O以及Ru-O化合物，且利用H_2O_2分解反應測試其觸媒活性，結果

顯示在 350℃下鍛燒之化合物的活性較佳，尤以Y-Ba-Cu-O化合物最好。在本研究中，空氣陰極是以混合漿料法製作成多孔性電極結構，所得之最佳製程為：擴散層成分由 60wt%碳黑與 40wt%PTFE組成，催化層則含 60wt%碳黑、20wt%催化劑與 20wt%PTFE，將擴散層與催化層疊壓在鎳網上。

本研究利用三種常用的電化學方法，包括定電流放電法、循環伏特安培法以及Tafel極化曲線分析，針對不同催化劑的空氣陰極進行測試，結果顯示在定電流放電法中以Co_3O_4、RuO_2、CuO在 350℃下鍛燒的效能最佳。以循環伏特安培法知其各空氣極產生氧化還原的電位。進行Tafel極化曲線分析顯示空氣極的電位不易達理論值，而受動力學控制，導致開路電壓相差達 0.3~0.65V；並顯示出氧還原及氧生成反應的性能，氧生成反應與表面積有很大的關係，導致純碳材的催化效能最佳。

A Study on the Transition-metal Oxide Catalysts for the Cathode of Zinc-Air Fuel Cell

Student：Ya-Jean Huang　　Adviser：Dr. Pang Lin

Department of Material Science and Engineering

National Chiao Tung University

Abstract

Metal-air fuel cells include the Zn-air and Al-air type fuel cells. They have been used as low-power portable electronics, because of their simple structure, high specific energy, low cost, stability and other advantages. To meet the future energy requirements of electrical motorcycles in this country, the cathode activities of the zinc-air fuel cells (or the reduction rate of O_2) should be boosted to a high specific energy/power. The reduction mechanism of O_2 in alkaline media prevails on the surfaces of conductive powders (e.g. carbon black loaded with an electrocatalyst) mixed in the cathode, which absorbs the reactants (O_2, H_2O and OH^-) and releases the products (OH^- and HO_2^-). The conductive powders act as the reaction carriers. The characteristics of cathode catalyst to facilitate the reduction of O_2 would be critical to the activity of the cathodes. For economical reasons, low-cost catalyst would be the choice for practical mass production.

This study is to stress on non-noble oxide catalysts. A series of the

transition metal oxides, La-Ca-Co-O, Y-Ba-Cu-O, Ba-Ru-O, Co-O, Cu-O and Ru-O compounds were prepared using the amorphous citrate precursor method. Catalytic activity for H_2O_2 decomposition reaction on all catalysts was found that the Y-Ba-Cu-O compound was calcined at 350℃ has better activity. The porous electrodes are made of slurry with various kinds of compositions. Manufacturing processes and optimal conditions for the air cathode are described as follow. The diffusion layer is consisted of 60wt% carbon black and 40wt% PTFE suspension, and the active layer is made of 60wt% carbon black, 20wt% catalyst and 20wt% PTFE suspension. The diffusion layer and the active layer are pressed together with a Ni net to form the air cathode.

The investigation is via the utilization of familiar electrochemical methods including the constant-current discharging measurement, the cyclic voltammetry and the Tafel polarization curves analysis. The various catalysts for air cathode were carried out the electrochemical testing. In the constant-current discharging measurement, the results show that the Co_3O_4, RuO_2 and CuO compound were calcined at 350℃ have the best catalytic effects. Over a wide potential range, cyclic voltammograms of the air cathode would be observed the redox peaks. The Tafel curve analysis indicates that the equilibrium potential of the air cathode is difficult to approach to the theoretical value and is under the control of kinetics. It leads to the OCV's difference of 0.3~0.65V for the air cathode. The resulting polarization curves show the performance of the oxygen reduction and oxygen evolution reaction. The electrode without catalyst was the most active in the oxygen evolution reaction which has relation to the specific surface area of carbon material.

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