$ZnMn_2O_4$ as a material for supercapacitors and its stability against the electrolyte.

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1. Abstract

The electrolyte is an essential part of a supercapacitor, conditioning its performance. Thus, the specific capacitance measured for the supercapacitor electrode in the typical three-electrode arrangement of an electrochemical cell is sometimes not reflected in the supercapacitor. For this reason, $ZnMn_2O_4$ electrodes have been manufactured by spray pyrolysis on ITO/glass. The electrodes have been characterized electrochemically, and in symmetrical supercapacitors in which three types of electrolyte have been used, studying the effect of the electrolyte on the stability of the electrode and the capacity of the supercapacitor.

2. Introduction

Supercapacitors (SCs) provide two energy storage mechanisms, the double-layer formed by the interface between electrodes and electrolyte, and through a Faraday pseudocapacitor process produced by rapid and reversible chemical adsorption-desorption or oxidation-reduction reactions. The SC electrochemical performance is directly related with the electrode-material, the surface area, the porosity, and the electrolyte. Manganese oxide base materials are used due to their high theoretical specific capacitance and excellent capacitive performance in an aqueous, multivalent electrolyte, low cost, and environmental friendliness. Manganese oxide (MnO_2) is one of the most widely used due to its large theoretical specific capacitance of 1370 F g^{-1}. to reduce or avoid the problems of low conductivity and the loss of soluble Mn^{2+}, Zn^{2+} is introduced. In this way, $ZnMn_2O_4$ spinel is a promising material for the manufacture of supercapacitor electrodes.

3. Experimental

$ZnMn_2O_4$ electrodes have been prepared by spray pyrolysis over commercial In_2O_3:Sn (ITO) glass. This deposition method drives the precursor solution from the syringe pump to the spray nozzle with the help of an air compressor. The atomized solution reaches the substrate which is hold at controlled temperature. The precursors were zinc and manganese acetate ($Zn(AC)_2·2H_2O$) and ($Mn(AC)_2·4H_2O$) dissolved in distillated water with concentrations of 0.005 M and 0.01 M respectively. The spray pyrolysis conditions were a flow rate of 20 ml min^{-1} and a substrate temperature of 400 ºC, while the deposition time varied from 2 to 15 minutes. The electrode size was: 2.5 cm x 4 cm. Three electrolytes of very different nature were used to build the supercapacitors: a membrane soaked in a water solution of sodium sulfate, lithium perchlorate in polyvinypyrrolidone (PVP), and an ionic liquid dissolved in PVP. Electrochemical performance of each individual electrode was measured in a typical three electrode system with a SCE as reference electrode and platinum as counter electrode. The electrochemical properties were investigated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

3. Body of the Abstract

It has been found that the specific capacity of the supercapacitor is generally lower than expected according to the values obtained in the electrochemical cell with three electrodes for the case of the use of aqueous solutions of sodium sulfate. An irreversible solubilization of Zn has been found with the transformation of spinel to manganese oxide in which sodium sulfate intervenes. In a comparative way, the aqueous electrolyte of sodium sulfate has been replaced by lithium perchlorate or ionic liquid, both in PVP, finding a greater stability of the electrode and an improvement in the specific capacity.

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