Available online at www.sciencedirect.com
ScienceDirect
Electrochimica Acta 52 (2006) 1451–1456
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Synthesis and electrochemical properties of layered $Li[Li_{(1/3-x/3)}Cr_xMn_{(2/3-2x/3)}]O_2$ prepared by sol–gel method

I. Ruth Mangani, C.W. Park, J. Kim *

Department of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, South Korea

Received 14 October 2005; received in revised form 1 February 2006; accepted 24 February 2006
Available online 9 June 2006

Abstract

The $Li[Li_{(1/3-x/3)}Cr_xMn_{(2/3-2x/3)}]O_2$ ($0.15 \leq x \leq 0.3$) cathode materials were synthesized by sol–gel process using aqueous solutions of metal acetates and citric acid as the chelating agent. The precipitate of metal citrate was dried in a vacuum oven for 10 h at 100 °C. After drying, the gel precursor was calcined at 300 °C for about 10 h. The resulted powder was ground and heated at 900 °C. The structural characterization was carried out by fitting the XRD data with Rietveld program. The samples exhibited a well defined layered structure and the unit cell parameters linearly increased with increasing chromium contents in $Li[Li_{(1/3-x/3)}Cr_xMn_{(2/3-2x/3)}]O_2$ Surface morphology was determined by SEM and HRTEM and it is found that the cathode material consisted of highly ordered single crystalline particles with layered-hexagonal structure. Test cells were assembled and cycled in the voltage range of 2.0–4.9 V with a current density of 7.947 mA/g. Electrode with ($x = 0.2$) delivered a high reversible capacity of around 280 mA h/g in cycling.

Keywords: Lithium batteries; Sol–gel method; Citric acid; Layered compound; Manganese; Chromium

1. Introduction

Various kinds of lithiated transition metal oxides such as spinel $LiMn_2O_4$, layered $LiCoO_2$ and $LiNiO_2$ have been widely investigated [1–3] as electrodes for lithium ion batteries. The layered $LiMnO_2$ are also of interest as cathode materials due to the properties of manganese based materials such as cost effective and non-toxic. But there is a severe fade in capacity of the layered $LiMnO_2$ due to the structural transition into spinel during cycling. This capacity fade makes the material undesirable for practical applications [4]. Attempts have been made to stabilize the layered structure by partially substituting manganese with other transition metal ion [5]. Recently, $Li[Li_{(1/3-x/3)}Cr_xMn_{(2/3-2x/3)}]O_2$ prepared via solution method was reported to exhibit good cycling retention [6].

Generally, lithiated transition metal oxides were synthesized by repeated grinding and firing the solid reactants at elevated temperatures (800–1000 °C). This method has many disadvantages such as inhomogenity, irregular morphology and larger particle sizes with a broader particle size distribution. In order to achieve the efficient lithium utilization, it is very necessary to obtain the submicron-sized particles with a uniform morphology, narrow size distribution and homogeneity [7–9]. In very recent years, development in synthesizing high performance cathode materials has been accomplished by wet chemistry method.

Sol–gel method is one of the wet chemistry synthesizing methods [10], can produce a highly homogenous submicron-sized particles with narrow particle size distribution in a relatively shorter processing time. These submicron-sized particles enable maximization of the particle surface area to volume ratio, the electrolyte–cathode material interfacial area and the particle to particle utilization uniformity during cycling and hence consequently improve the performance of the cathode materials and enhance the battery performance [11–14].

To achieve the enhanced battery performance, we have prepared the $Li[Li_{(1/3-x/3)}Cr_xMn_{(2/3-2x/3)}]O_2$ ($0.15 \leq x \leq 0.3$) cathode material by citric acid assisted sol–gel method and study the structural and electrochemical properties.

* Corresponding author. Tel.: +82 62 530 1703; fax: +82 62 530 1699.
E-mail address: jaekook@chonnam.ac.kr (J. Kim).

0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.02.046

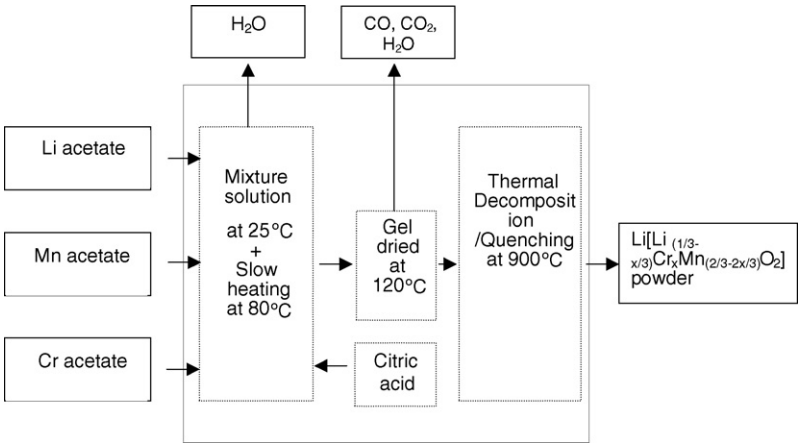

Fig. 1. Flow chart of citric acid assisted sol–gel method.

2. Experimental

2.1. Synthesis of $Li[Li_{(1/3-x/3)}Cr_xMn_{(2/3-2x/3)}]O_2$ ($0.15 \leq x \leq 0.3$) by sol–gel technique

The cathode materials were prepared by the sol–gel method using citric acid as the chelating agent. Aqueous solutions of lithium, manganese and chromium acetates were taken in stoichiometric amounts and dissolved in deionized water. This mixed solution was added with citric acid in desired proportion. The pH of the mixed solution was maintained between 6.5 and 7 by the ammonium hydroxide solution. The solution was stirred for 5 h to ensure that the reaction reagents were uniformly mixed and the complex reaction between Mn^{3+} and citric acid was accomplished. In this method the aqueous solution of complexing agent and the metal acetate salts turn to gel on evaporation of the solvent. Then the precipitate of metal citrate was dried in a vacuum oven for 10 h at 100 °C. On heating up to the decomposition point of the complex the organic components are eliminated as forms of CO_2 and H_2O. The abrupt formation of these gases bloats the material and greatly expands its structure to produce an ash-like morphology. Sometimes the decomposed compound itself is pure but in some other cases it contains impurities and hence the as-prepared LT-compounds need further heat treatment to achieve purity. The gel precursor was calcined at 300 °C for about 10 h. The resulted powder was ground well with agate mortar and quenched at 900 °C to gain crystallinity. Fig. 1 shows the flow chart of the sol–gel method.

2.2. Instrumentation

Thermal gravimetric analysis (TGA/DTA) of the precursor powder was done on a SDT Q600 V8.0 Build 95 thermal analyzer at a heating rate of 10 °C/min from room temperature to 900 °C in air. The powders were identified by X-ray diffraction (XRD) using a D/MAX Ultima III, Rigaku, Japan with Cu Kα radiation (λ = 1.54056 Å) and the lattice parameters were derived using the Rietveld method. The morphology of the samples was examined by scanning electron microscopy (JSM, 5400-JEOL) and transmission electron microscopy (HRTEM) using Philips, Tecnai F20. The elemental composition of the prepared cathode powders was determined by inductively coupled plasma (ICP), using the Perkin-Elmer 4300 DV analyzer.

The electrochemical performance of the prepared cathode materials was determined in galvanostatic cycling experiments. The test cells were assembled in an argon atmosphere. The electrolyte consists of 1 M $LiPF_6$ with ethylene carbonate and diethyl carbonate. The cathode materials were mixed with carbon and binder in the appropriate weight ratio of (85:10:5). The cell was tested in the voltage range of 4.9–2.0 V with a current density of 7.947 mA/g.

3. Results and discussion

3.1. Thermal analysis

Fig. 2 shows the TG/DTA curves of $Li[Li_{(1/3-x/3)}Cr_xMn_{(2/3-2x/3)}]O_2$ ($0.15 \leq x \leq 0.3$), prepared by sol–gel method, which display the formation of the layered phase of the precursor materials. There is a small weight loss in the temperature range of 180–200 °C. This weight loss is attributed to the superficial water loss due to the hygroscopic nature of the cathode precursor. The

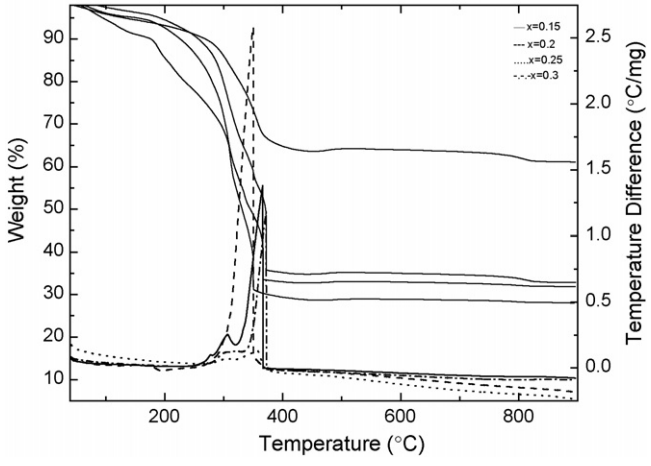

Fig. 2. TG/DTA curves of $Li[Li_{(1/3-x/3)}Cr_xMn_{(2/3-2x/3)}]O_2$ ($0.15 \leq x \leq 0.3$) powders prepared by the sol–gel method.