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Facile synthesis of copper-manganese spinel anodes with high capacity and cycling performance for lithium-ion batteries

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ABSTRACT

Copper-manganese spinel containing anodes were synthesized by a facile sol-gel method and evaluated in lithium-ion battery applications for the first time. The synergistic effects between copper-manganese and the aqueous binder (sodium carboxymethyl cellulose) provided a high specific capacity and excellent cycling performance. It was found that the specific capacity of the copper-manganese spinel remained at 608 mAh g^{-1} after 100 cycles at a current density of 200 mA g^{-1}. Furthermore, a relatively high reversible capacity of 278 mAh g^{-1} could be obtained at a current density of 2000 mA g^{-1}, indicating a good rate capability. These studies suggest that copper-manganese spinel is a promising material for lithium-ion battery applications due to a combination of good electrochemical performance and low cost.

1. Introduction

With the energy demands for portable electronic devices, electric vehicles and hybrid electric vehicles on the rise, interest in commercial lithium-ion batteries (LIBs) using carbon materials as anodes has increased [1,2]. However, the lower theoretical capacity of carbon anodes limits the development of LIBs. Due to this, the desire for novel materials with high capacity is exceedingly strong and therefore it is no surprise that transition metal oxides (TMOs) have attracted many scientists' attention due to their high energy density.

Single TMOs (M_xO_y, M=Co, Fe, Mo etc.) have been studied as anode materials because of their high theoretical capacity on the basis of the following conversion mechanism [3]:

$$M_xO_y + 2yLi^+ + 2ye^- \leftrightarrow yLi_2O + xM\ (M = Co,\ Fe,\ Mo,\ etc.)$$

However, volume expansion and poor electrical conductivity result in fast capacity fading and poor rate capability during cycling [4]. Solutions to this problem have centered on the search for new materials with advantageous structures and the use of new binders. During recent years, mixed TMOs, e.g. $ZnMn_2O_4$, $CuFeO_2$, $CuCo_2O_4$, $CoMn_2O_4$, have attracted lots of attention due to improved electrochemical performance resulting from synergetic effects [5,6] and higher electrical conductivity than that of single TMOs [7]. In addition to their application as battery anodes TMOs have been reported in catalysis and here copper-manganese spinel (CMS) has been widely applied e.g. the oxygen reduction reaction (ORR) and total oxidation of ethanol. Such materials should also be suitable for battery systems yielding excellent electrochemical performance, environmental friendliness and low cost, however their use as anodes in LIBs has not, to our knowledge, yet been reported.

In this paper we report the synthesis of copper-manganese spinel ($Cu_{1.3}Mn_{1.7}O_4$) by a facile sol-gel method. This is then evaluated in terms of its electrochemical performance which shows a high specific capacity and excellent cycling performance when used as an anode material in lithium-ion batteries.

2. Experimental section

Nanostructured $Cu_{1.3}Mn_{1.7}O_4$ powder (CMO) was synthesized by an improved sol-gel method. In a typical synthesis, 30 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ in a molecular ratio of

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1.3:1.7 and glycine (10 g) were dissolved in 500 mL of deionized water under vigorous stirring in a bath to 80 °C. Then citric acid (10 g) was slowly added until a viscous gel was formed. The viscous gel was combusted in air at 250 °C for 1 h. The residual powder was carefully ground by ball-milling and then sintered in air at 600 °C for 5 h.

In order to characterize the powder, X-ray diffractometer (XRD, Rigaku Ultima IV), transmission electron microscopy (TEM, JEOL JEM-2001F), X-ray photoelectron spectroscopy (XPS, Physical Electronics 5400 ESCA) and TG/DTA 6200 (Seiko) apparatus were used. The electrochemical performance was conducted using 2025-type coin cells on a Land CT2001A test system (Wuhan, China). The electrode was prepared by coating the slurry, composed of a mixture of 70 wt% active materials, 20 wt% Super-P and 10 wt% sodium carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR) with a weight ratio of 1:1, onto Cu foil. The electrolyte was the mixture of ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (weight ratio of 1:1:1) with 1 M $LiPF_6$.

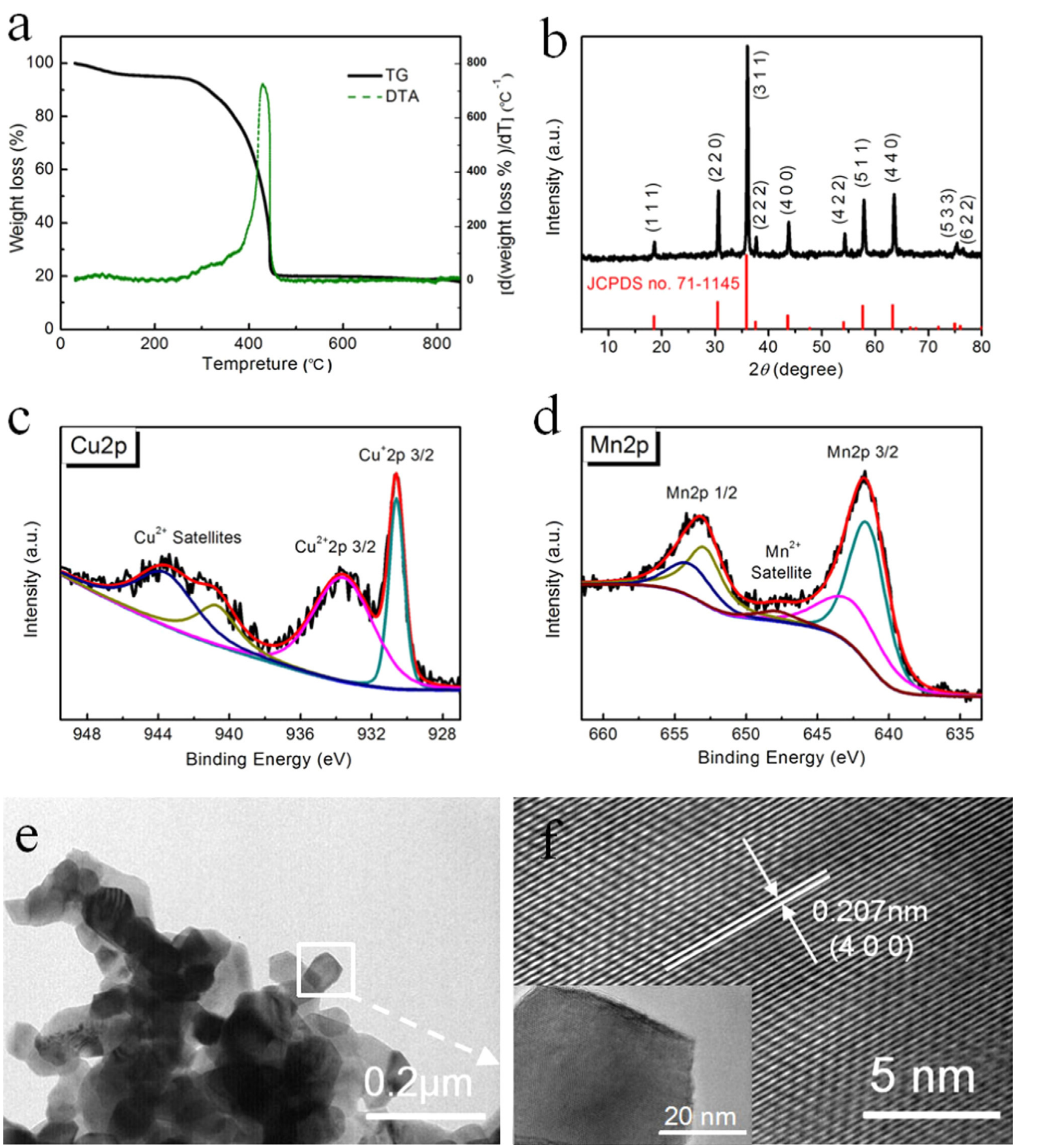

Fig. 1. (a) TG/DTA curves of the precursor, (b) XRD patterns of CMO, (c and d) XPS spectra of Cu 2p and Mn 2p and (e and f) TEM and HRTEM images of CMO.