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SYNTHESIS OF $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ ($x \sim 0.18$) BY GLYCINE-NITRATE METHOD

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Abstract

$\text{LiCr}_{0.18}\text{Mn}_{1.82}\text{O}_4$ spinel has been successfully synthesized by glycine-nitrate method. As a cathode material for lithium batteries it shows initial discharge capacity of 107.1 mAh/g and capacity retention of 93.3% after ten cycles.

Introduction

LiMn_2O_4 is a promising cathode material for ion-lithium batteries because it delivers high voltage, good capacity and it is a low cost and non toxic material. Unfortunately LiMn_2O_4 spinel shows considerable decrease in capacity during electrochemical charging-discharging on the 4V plateau. Recently several dominant modes of capacity fade have been proposed: Mn-dissolution and concomitant Li-for-Mn ion exchange at the end-of-discharge, and development of microstrain between two cubic phases formed during cycling [1,2]. The largest improvement in preventing capacity fade has been achieved by substitution of some manganese by other metal cations. These more robust spinels have higher average oxidation state of remaining manganese ($>3.5+$). This leads to a lower theoretical capacity because of the lower number of lithium ions that can be extracted from the spinel structure before all manganese is oxidized. Not only the choice of M^{z+} metal cation type but also its amount "x", is important for obtaining $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ cathode material with adequate initial capacity and high capacity retention. Cr^{3+} is among the cations whose substitution for manganese gives best performance increase especially for $x = 0.175$ [1,3,4]

$\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ spinels are usually prepared by time and energy consuming solid state reaction, starting from carbonates and/or oxides [1-3,5]. In this work we tried to synthesize $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$ ($x \sim 0.18$) powder material by rapid glycine-nitrate method developed before for synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics [6].

Experimental

1 M aqueous solutions of LiNO_3 , $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were prepared from p.a. chemicals. They were mixed in appropriate ratio so the total volume was 30-40 ml. Glycine was added in the mixture either as a solid or as a water solution. Its role was to serve both as a fuel for combustion and as a complex ant to prevent inhomogeneous precipitation of individual components prior to combustion. Amount of glycine was such to make glycine-to-nitrate molar ratio equal to 1.2. Precursor solution was placed in a covered glass beaker and heated in an oven at 200°C

until spontaneous ignition occurred. Ash resulting from combustion was heated at 800°C for 4 hours.

The XRPD experiments were done with the $\text{CuK}\alpha_{1,2}$ radiations in 15-70° 2 θ range with the 0.05° step and 2 seconds exposition time.

Electrochemical experiments were performed in a cell filled with argon. Electrolyte was 1 M LiClO_4 in PC and EC mixture (1:1 mole ratio). Before dissolving p.a. LiClO_4 was dried under vacuum at 120-140°C for at least 2 hours. PC and EC were distilled twice under vacuum, and both times middle $\frac{2}{3}$ fraction was collected. Working electrode was made from synthesized material, "Vulcan" carbon black and PVDF mixed in 90:5:5 weight percent ratio and deposited on platinum foil from slurry prepared in N-Methyl-2-Pyrrolidone. Active cathode material weighted 3.9 mg and was spread over 1.7 cm² of Pt-foil surface area. Two glass tubes filled with lithium metal were used as double counter electrode.

Results and Discussion

All reflections of obtained XRPD pattern correspond to pure spinel phase. Small shifts in 2 θ values exist for all reflections comparing to LiMn_2O_4 diffraction pattern. Lattice parameter $a = 8.223 \text{ \AA}$ has a lower value than for LiMn_2O_4 ($a = 8.241-8.249 \text{ \AA}$) [1,2,7]. This lattice contraction indicates that chromium-ion is incorporated into spinel manganese oxide [8] and a more complex oxide $\text{LiCr}_{0.18}\text{Mn}_{1.82}\text{O}_4$ is formed.

For potential application the most important thing is to have acceptable electrochemical behavior of obtained cathode material. So we checked cycling characteristics of $\text{LiCr}_{0.18}\text{Mn}_{1.82}\text{O}_4$ by charging electrochemical cell to 4.3 V and discharging to 3.3 V. Quite high current rate C/3 has been chosen. Current density was 112 $\mu\text{A}/\text{cm}^2$. Ten cycles have been recorded. Fig.1 shows relationship between discharge capacity and cycle number for our $\text{LiCr}_{0.18}\text{Mn}_{1.82}\text{O}_4$ comparing to LiMn_2O_4 prepared by solid state reaction and cycled at C/15 current rate [1]. Discharge capacity of $\text{LiCr}_{0.18}\text{Mn}_{1.82}\text{O}_4$ synthesized by glycine-nitrate method changes from 107.1 in the first to 99.9 mAh/g in the tenth cycle. LiMn_2O_4 [1] although cycled with five times lower current rate decreases a discharge capacity from 108.6 to 73.3 mAh/g in the first ten cycles. The capacity retention of $\text{LiCr}_{0.18}\text{Mn}_{1.82}\text{O}_4$ is 93.3% comparing to that of only 67.5% for LiMn_2O_4 . As a conclusion it may be said that $\text{LiCr}_{0.18}\text{Mn}_{1.82}\text{O}_4$ is successfully synthesized by a rapid combustion method delivering very good cyclability as a cathode material for lithium batteries.

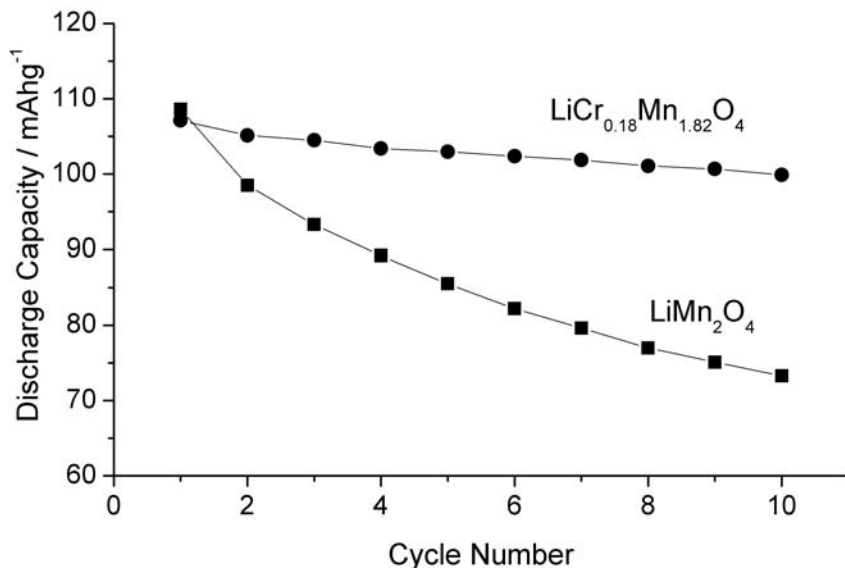


Figure 1. Discharge capacity of $\text{LiCr}_{0.18}\text{Mn}_{1.82}\text{O}_4$ (glycine-nitrate method) and LiMn_2O_4 (solid state reaction [1]) versus cycle number.

References

- [1] M. C. Tucker, J.A. Reimer, E.J. Cairns, *J. Electrochem. Soc.*, 2002, 149(5), A574.
- [2] Y. Shin, A. Manthiram, *J. Electrochem. Soc.*, 2004, 151(2), A204.
- [3] C. Sigala, D. Guyomard, Verbaere, Y. Piffard, M. Tournoux, *Solid State Ionics*, 1995, 81, 167.
- [4] C-H. Lu, Y. Lin, H-C. Wang, *J. Mater. Sci. Lett.*, 2003, 22, 615.
- [5] R. Koksang, J. Barker, H. Shi, M. Y. Saïdi, *Solid State Ionics*, 1996, 84, 1.
- [6] L. R. Pederson, G. D. Maupin, W. J. Weber, D. J. McReady, R. W. Stephens, *Mat. Lett.*, 1991, 10, 437.
- [7] D. Jugović, M. Mitrić, N. Cvjetičanin, M. Miljković, V. Jakanović, D. Uskoković, *Mater. Sci. Forum*, 2004, 453-454, 387.
- [8] M. C. Tucker, J.A. Reimer, E.J. Cairns, *J. Electrochem. Soc.*, 2001, 148(8), A951.