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SYNTHESIS AND ELECTROCHEMICAL BEHAVIOUR OF COPPER DOPED MANGANATE AND COBALTATE CATHODE MATERIALS FOR LITHIUM BATTERIES

S DEEPA, N S ARVINDAN, C SUGADEV, R TAMILSELVI, M SAKTHIVEL
A SIVASHANMUGAM AND GOPUKUMAR

Central Electrochemical Research Institute, Karaikudi 630 006, INDIA

Synthesis and characterization of $LiCu_{0.05}CO_{0.95}O_2$ and $LiCu_{0.05}Mn_{1.95}O_4$ were carried out in order to improve the electrochemical properties of $LiCoO_2$ and $LiMn_2O_4$ for lithium secondary cells. Single phase $LiCu_{0.05}CO_{0.95}O_2$ and $LiCu_{0.05}Mn_{1.95}O_4$ were obtained by heating a reaction mixture of $LiOH.H_2OCu(NO_3)_2.3H_2O$ and $CO(CH_3COO)_24H_2O$ at 723 K for 3 hrs and $Li(CH_3COO).2H_2O$, $Cu(NO_3)_{2.3H_2}O$ and $Mn(CH_3COO)_2.4H_2O$ at 1346 K for 3 hrs respectively. Structural studies were done using X-ray diffraction method. Phase purity was established using the differential thermal and thermogravimetric analysis. Lithium button cells were fabricated using lithium foil as anode, $LiCu_{0.05}CO_{0.95}O_2$ and $LiCu_{0.05}Mn_{1.95}O_4$ cathodes in $LiAsF_6$/EC/DEC as electrolyte. Charge and discharge behaviour was studied for the above cells.

Keywords:

INTRODUCTION

Lithium intercalated transition metal oxides are the most attractive cathode materials in lithium ion cells, because of their high capacity and operating voltage. Among the transition metal oxides, the electrochemical properties of doped manganate and cobaltate cathode materials have been studied extensively over last decade. Research efforts are mainly focussed on improving the capacity and cyclability of the electrode by introducing changes in their preparation procedure and synthesis temperature. Although the technology of ambient temperature rechargeable Lithium ion cells has emerged only recently, there is an abundance of materials suitable for fabricating positive electrodes. As is clear from the above, the most favourable approach to secondary lithium cells in the near future is to use as insoluble positive electrode.Among these the transition metal oxides with layered structures, and the transition metal oxides with three-dimensional net work structures. A feature of all except a few of these materials is that the positive electrode reaction involves an intercalation or a topotactic reaction. An ideal intercalation reaction involves the interstitial introduction of guest species into a host lattice without structural modification of the host. Such reaction is reversible because similar transition states are readily achieved for both the forward and reverse reactions, leading to close compliance with the thermodynamic principle of microscopic reversibility.

$$X\,Li^+ + xe^- + My_n \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_xMy_n$$

The criteria (structure/property relationships) for intercalation compounds to be used as positive electrodes

* must be an intercalation host for lithium.
* low fermi level and Li+ site energy-high OCV.
* electrode potential varies little with lithium content- cell voltage varies with state of charge
* capable of accomodating large quantities of lithium per formula unit-high capacity
* low formula mass-high gravimetric energy density
* low molar volume-high volumetric energy density
* sustain high rates of lithium intercalation and deintercalation-high cell discharge/charge rates

* high reversible Lithium intercalation-Charge/discharge cycles
* stable in contact with candidate electrolyte
* avoid co-intercalation of solvent.

EXPERIMENTAL

Coin cells of 2016 size were fabricated as indicated below:

* Anode:Lithium Metal
* Cathode: $LiCu_{0.05}Mn_{1.95}O_4$
  $LiCu_{0.05}CO_{0.95}O_2$
* Electrolyte: 1 *M* $LiASF_6$ in EC:DEC
* Separator: polypropylene sheet
* Testing : Galvanostatic cycling

Synthesis of doped cathode material

Among the various cathode materials doped cathode materials play a vital role in rechargeable lithium batteries. These materials could be prepared by using thermal methods by mixing a stochiometric quantities of the corresponding salts and subjecting a resulting mixture to the thermal treatment.

Synthesis of $LiCu_{0.05}Mn_{1.95}O_4$

The cathode material $LiCu_{0.95}Mn_{1.95}O_4$ was prepared by thermal methods by mixing a molar ratios of $Li(CH_3COO).2H_2O$. $Cu(NO_3)_2.3H_2O$ and $Mn(CH_3COO)_2.4H_2O$ according to the desired stoichiometry the composite salt mixture containing the following quantity of the material

$Li(CH_3COO).2H_2O$——5.101g

$Cu(NO_3)_2.3H_2O$——0.6g

$Mn(CH_3COO).4H_2O$——12.2g

The above materials were heated in a furnace at 1073 K for 3 days and it was then subjected to 10 hr pulverization.

Synthesis of $LiCu_{0.05}CO_{0.95}O_2$

The synthesis of cathode material $LiCu_{0.05}CO_{0.95}O_2$ was done by thermal methods by mixing molar ratios of $LiOH.H_2O$, $Cu(NO_3)_2.3H_2O$ and $Co(CH_3COO)_2.4H_2O$ according to the desired stoichiometry. The composite salt mixture was containing the following quantity material.

$Co(CH_3COO).4H_2O$——11.8311g

$Cu(NO_3)_2.3H_2O$——0.6g

$LiOH.H_2O$——2.1g

The materials were mixed and heated in a furnace for 1073 K for three hrs and it was pulverized for 8-10 hours.

TABLE I: Comparison of the observed XRD data ($LiCu_{0.05}Mn_{1.95}O_4$) and the standard table

$2\theta_{obs}$	d_{lit} (Å)	d_{ots} (Å)	h	k	l
18.7160	4.752	4.7369	1	1	1
21.7502	4.115	4.0828	2	0	0
36.3392	2.481	2.4702	3	1	1
38.0122	2.376	2.3653	2	2	2
44.1879	2.058	2.0479	4	0	-
48.3629	1.888	1.8804	3	3	1
58.5050	1.584	1.5763	5	1	1
64.2889	1.455	1.4477	4	4	0
67.6005	1.391	1.3846	5	3	1
68.8972	1.372	1.3617	4	4	2

RESULTS AND DISCUSSIONS

XRD studies

The prepared samples were ground well and x-ray diffraction studies were carried out on the synthesized product, $LiCu_{0.05}Mn_{1.95}O_4$ to monitor the phase purity and structural nature of the prepared material. The Table I provide the indexing of the peaks assuming a face centered cubic structure. The lattice constant of the single-phase product was found to be a = 8.19 which is very close to the literature data a = 8.23 Å.

Similarly, XRD analysis was carried out on the synthesized $LiCu_{0.05}CO_{0.95}O_4$ to monitor the phase purity and structure

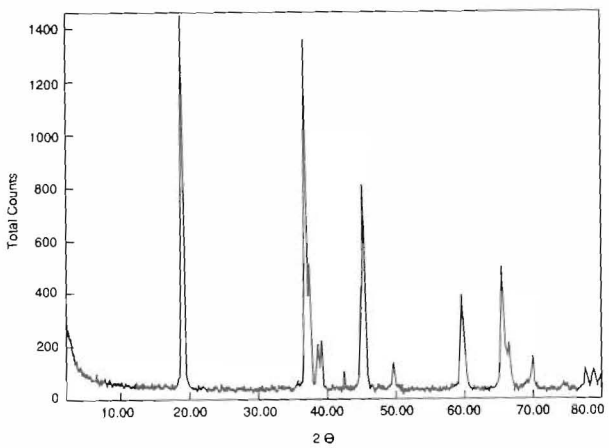

Fig. 1: XRD spectrum of $LiCu_{0.05}Co_{1.95}O_2$

TABLE II: Comparison of observed XRD data and the standard table

$2\theta_{obs}$	d_{lit} (Å)	d_{obs} (Å)	h	k	l
18.9438	4.693	4.6808	0	0	3
37.3930	2.403	2.4030	1	0	1
38.5450	2.347	2.3338	0	0	6
39.0458	2.304	2.3050	1	0	2
45.2527	2.005	2.0020	1	0	4
49.4631	1.844	1.8412	1	0	5
59.4424	1.552	1.5537	1	0	7
65.2951	1.427	1.4278	1	0	8
68.2815	1.408	1.4090	1	1	0
69.6983	1.349	1.3480	1	1	3

of the prepared material. The Fig. 1 shows the XRD diffractogram and the Table II provides the indexing of the peaks assuming a hexagonal structure. Later analysis provides a near fitting of the data of the prepared material (a = 2.82) with regard to literature data value (a = 2.816). The slight variations in the lattice parameters may be attributed to the copper doping in the lithium cobaltate.

TGA/DTA analysis

The figure shows the TGA/DTA Plot of the synthesised $LiCu_{0.05}Mn_{1.95}O_4$. In the DTA, a steady exothermic curve rising upto 583 K suggests that the oxidation of the sample. A corresponding decrease in the mass percent of about 1.2% in the TGA curve may be attributed to the loss of moisture and volatile matter. Further increase in temperature undergoes an endothermic profile of the DTA up to 1073 K suggesting the single phase formation of the above compound duly complemented by a slow attainment of a flat mean percent profile in the TGA.

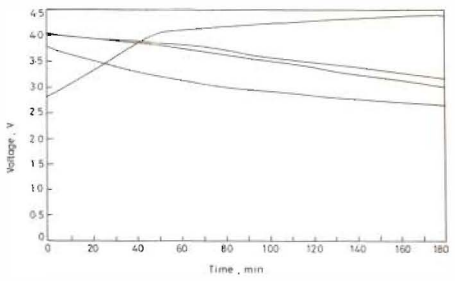

Fig. 3: Charge-discharge characteristics of $Li/LiCu_{0.05}Co_{0.95}O_2$ cell

Testing of the fabricated cells

The fabricated cells were subjected to charge/discharge cycles at a constant current of 0.5 mA. The charge/discharge characteristics of the individual cells are presented in Figs. 3 and 4. The OCV of the cells are as follows:

Compounds	OCV
$Li/LiCu_{0.05}Mn_{1.95}O_4$cell	3.10 V
$Li/LiCu_{0.05}CO_{0.95}O_2$cell	2.94 V

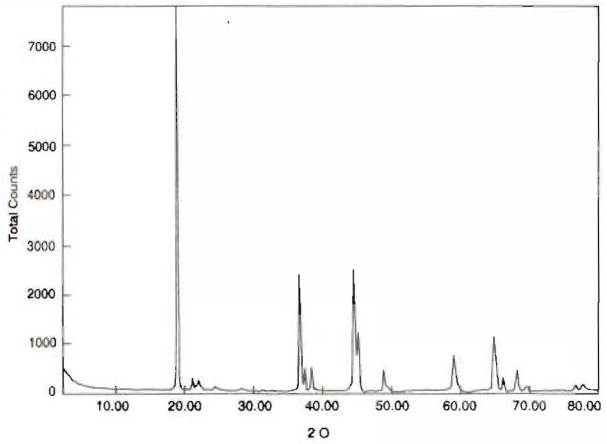

Fig. 2: XRD spectrum of $LiCu_{0.05}Mn_{1.95}O_4$

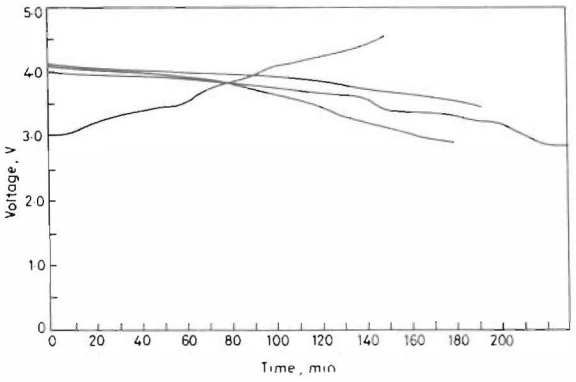

Fig. 4: Charge-discharge characteristics of $Li/LiCu_{0.05}Mn_{1.95}O_4$ cell

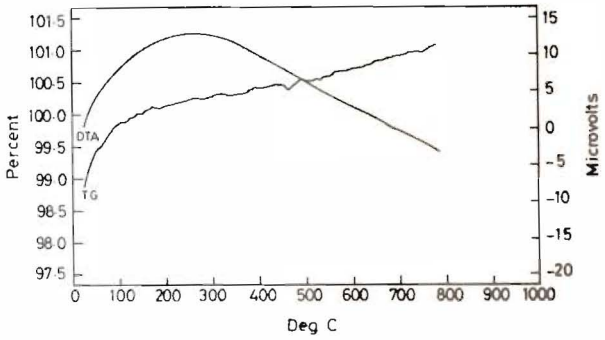

Fig. 5: Thermal spectrum of $LiCu_{0.05}Mn_{1.95}O_2$

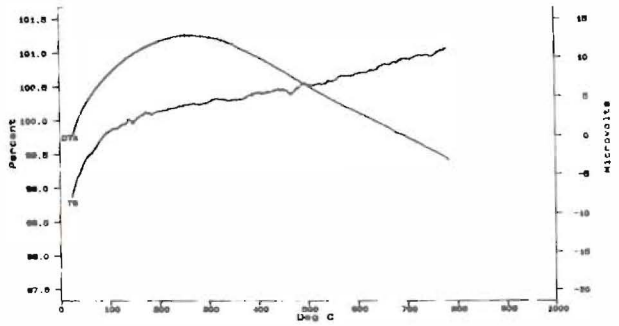

Fig. 6: Thermal spectrum of $LiCu_{0.05}Co_{1.95}O_4$

CONCLUSION

$LiCu_{0.05}Mn_{1.95}O_4$ and $LiCu_{0.05}CO_{0.95}O_2$ powders were prepared and cathodes for Lithium rechargeable cells were made from them. 2015 type cells fabricated using Lithium anode, the prepared material, in an electrolyte comprising of 1 *M* $LiASF_6$ in 50% EC/DEC, employing a polypropylene separator. Charge discharge characteristics suggest improvement in cycles by doping. The improvement of cycle performance in $LiMn_2O_4$ was obtained at a slight expense of capacity, which is attributed to the stabilisation in the spinel structure by doping and the small volume changes during the extraction-insertion of lithium. This work suggests that it is possible to fabricate Lithium rechargeable cells using copper doped cathode material.

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