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Solid State Ionics 175 (2004) 291-295



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Cycling behavior of LiNi_xCo_yMn_{2-x-y}O₄ prepared by sol-gel route

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Abstract

Spinel LiNi_xCo_yMn_{2-x-y}O₄ (where x=y=0.1,0.01) compounds were prepared through sol-gel method using glycine as the chelating agent. The prepared compounds were subjected to XRD, SEM, TG/DTA, cyclic voltammetry, charge-discharge and AC impedance spectroscopy studies. The formation of the compound was well substantiated by X-ray diffraction studies. The prepared LiNi_{0.01}Co_{0.01}Mn_{1.98}O₄ compound offers better coloumbic efficiency and cyclability than LiNi_{0.1}Co_{0.1}Mn_{1.8}O₄. Also, the theoretical capacity of multidoped manganese oxide was calculated and is compared with experimentally obtained one. © 2004 Elsevier B.V. All rights reserved.

PACS: Materials Science 81.05.Zx New Materials: theory, design and fabrication *Keywords:* LiMn₂O₄; Multidoped spinel; Cyclability; Coloumbic efficiency

1. Introduction

LiMn₂O₄ is currently found to be a potential candidate as cathode material for applications in lithium batteries due to its high theoretical capacity, excellent electrochemical reversibility, good voltage regulation on cycling, eco-friendliness and low cost [1,2]. The synthetic method employed plays an important role on the electrochemical properties of LiMn₂O₄. The solid-state reaction, which consists of extensive mechanical mixing and extended grinding, also leads to the detrimental quality of the final products. This condition leads to inhomogeneity, irregular morphology, larger particle size and poor stoichiometry. In order to avoid these problems, sol-gel method has been employed, which is a desirable method to obtain cathode materials with good homogeniety and uniform morphology. However, its capacity fades upon prolonged cycling, especially at elevated temperature, still remains a problem area [3].

This fade in capacity upon prolonged cycling is attributed to Jahn–Teller distortion [3], dissolution of spinel

into the electrolyte and decomposition of the electrolyte [4], oxidation of electrolyte [5], lattice site exchange between lithium and manganese ions and particle disruption [6]. It has been demonstrated by many researchers that partial substitution of manganese with metal ion may stabilize the spinel structure of the host compound [7]. Single-ion-doped LiMn₂O₄ spinels could not rectify all these problems. Amine et al. [8] have reported LiNivMn2-vO4 materials which exhibited electrochemical activity in the 5-V region. The higher capacity in the nickel-substituted material was attributed to the oxidation of Ni2+ to Ni4+. Nickelsubstituted LiMn₂O₄ was also used as a cathode material in a cell comprising Cu-Sn microcomposite anode [9]. Hosoya et al. [10] reported cycling behavior of Co- or Nisubstituted LiMn₂O₄. The effect of multiple cation-substituted LiMn₂O₄ has also been reported in the recent years. As stated in Ref. [7], LiNi_vCu_{0.05-v}Mn_{2-v}O₄ was found to exhibit superior high potential cathodic properties. Also, Co- and Ni-doped LiMn₂O₄ thin film has been studied by Streibel et al. [11]. Very recently, Kawai et al. [12] have reviewed high voltage materials for lithium batteries.

This paper reports the synthesis of multidoped Ni and Co $LiMn_2O_4$ cathode at different stoichiometric levels and their structural and electrochemical properties as an intercalating cathode material for lithium batteries. Also, the theoretical

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capacity was calculated for the multidoped $LiMn_2O_4$ and was compared with experimentally obtained one.

2. Experimental procedure

The LiNi_xCo_yMn_{1.98}O₄ (x=y=0.01, 0.1) spinel compound was prepared through sol–gel method using glycine as the chelating agent. Stoichiometric mixtures of Li(NO₃), Co(NO₃)₂ · 6H₂O, Mn(NO₃)₂ · 4H₂O and Ni(NO₃)₂ · 6H₂O were dissolved in double distilled water and added drop wise to a continuously stirred aqueous solution of glycine solution. The resultant solution was evaporated at 70–80 °C until a sol–gel was obtained. The resulting gel precursor was decomposed in air and calcinated at 800 °C in air for 10 h.

The compound was subjected to XRD, SEM analysis. The TG/DTA traces for the precursor were studied. The contents of Li, Ni, Co and Mn were determined by means of ICP-AES. The charge–discharge studies were performed in test cells. The lithium metal was used as an anode. The electrolyte was 1:2 mixture (v/v) of EC and DMC containing 1 M of LiPF₆.

2.1. Calculation for theoretical capacity

For the 1st compound, i.e., Li $Ni_{0.01}Co_{0.01}Mn_{1.98}O_4$, it can be written as Li(I) Ni (II) 0.01Co(III) 0.01 Mn(III) 0.97 Mn(IV) (1.01) O₄, and hence, the molecular weight will be 181.58 g. In this logic, Co and Mn are active in the 3.6–4.2 V range. Ni present as Ni(II) is active only in the 4.6–4.9 V range, i.e., in the 5 V region. So according to the calculation, capacity attributed to the oxidation of Co(III) and Mn(III) ions to Co(IV) and Mn(IV) ions, respectively, will be 147 mAh/g. Similarly for the second sample, the capacity will be 144 mAh/g.

3. Results and discussions

Fig. 1(a) and (b) shows the X-ray pattern of LiNi_{0.01} $Co_{0.01}Mn_{1.98}O_4$ and LiNi_{0.1} $CO_{0.1}Mn_{1.8}O_4$, respectively, calcinated at 800 °C for 10 h in air. The diffraction peaks are much sharper, the widths of the peaks are narrower and the positions which indicate an increase in crystallinity and formation of single phase are confirmed. All the peaks are indexable in the Fd3m space group to a cubic lattice, and the lattice parameter 'a' was calculated using a least square fit for LiNi_{0.01}Co_{0.01}Mn_{1.98}O₄ and LiNi_{0.1}Co_{0.1}Mn_{1.8}O₄ and are found to be 8.2211 and 8.5067 A°, respectively. The increase of 'a' value in the substituent ion concentration in LiMn₂O₄ is a characteristic feature of solid solutions that obey Vegard's law, which says some material parameters, e.g., lattice constants, vary with the mole fraction of the substituent species [13].

Scanning electron micrographs of the spinel $\text{LiNi}_{0.01}$ Co_{0.01}Mn_{1.98}O₄ and $\text{LiNi}_{0.1}$ Co_{0.1}Mn_{1.8}O₄ are shown in Fig. 2(a) and (b), respectively. It is observed from Fig. 2(a)



Fig. 1. Powder X-ray diffractograms of (a) $LiNi_{0.01}Co_{0.01}Mn_{1.98}O_4$ and (b) $LiNi_{0.1}Co_{0.1}Mn_{1.8}O_4.$

that the size of the particles is around 1–10 μ m similar to a cubic gold crystal. The LiNi_{0.01}Co_{0.01}Mn_{1.98}O₄ stoichiometric spinel has smaller and uniformly sized particles as compared to LiNi_{0.1}Co_{0.1}Mn_{1.8}O₄ stoichiometry where the particles are agglomerated and larger in size. Fig. 3 shows the TG/DTA traces of LiNi_xCo_yMn_{2-x-y}O₄ gel precursor at a heating rate of 10 °C/min in air. The weight loss in the temperature range of 50–100 °C corresponds to the removal of superficial and structural water in the gel precursor which is accompanied by an endothermic peak in the DTA curve. The weight loss around 260 °C corresponds to the combustion of inorganic and organic constituents in the gel precursor [14]. Further, no weight loss was observed beyond 400 °C, which indicates the formation of the compound.

The cycling voltammograms were recorded for LiNi_{0.01} $Co_{0.01}Mn_{1.98}O_4$ and LiNi_{0.1} $Co_{0.1}Mn_{1.8}O_4$ between 3 and 4.2 V and are presented in Fig. 4(a) and (b), respectively. The two peaks in the range of 4 to 4.2 and 3.8 to 4 V correspond to a two-step lithium intercalation/deintercalation process into/ from 8a tetrahydral sites in the redox process of Mn^{3+}/Mn^{4+} couple. This behavior is similar to Li/LiMn₂O₄ cells where



Fig. 2. SEM images of (a) $LiNi_{0.01}Co_{0.01}Mn_{1.98}O_4$ and (b) $LiNi_{0.1}Co_{0.1}Mn_{1.8}O_4.$

two-step lithium intercalation/deintercalation process takes place at 4.0 and 4.1 V, which was reported to be induced by lithium ion ordering in the 8a tetrahedral sites [15]. This is in contrast to the behavior in Li/LiCr_{0.05}Mn_{1.95}O₄ cells where one dominant peak with the equilibrium voltage at 4.0 V and with a peak shoulder at 4.0 V; the broad oxidation/reduction peaks indicate that the lithium intercalation/deintercalation process is much more sluggish than that in other spinel



Fig. 3. TG/DTA traces of precursor (1) DTA (2) TG.



Fig. 4. Cyclic voltammograms of (a) $LiNi_{0.01}Co_{0.01}Mn_{1.98}O_4$ and (b) $LiNi_{0.1}Co_{0.1}Mn_{1.8}O_4.$

compounds. When the dopant Co or Ni content increases, the intensity of the peaks diminishes and the redox potential slightly decreases (Fig. 4b). The diminished intensity of the peaks may be due to the difficulty in the extraction/insertion of lithium from/in the double doped spinels during the charge-discharge stages. This also suggests that as the dopant concentration increases, the capacity also decreases, which is in agreement with our results. As suggested in Ref. [16], only Mn^{3+} are the active ions in this potential region. In the present case, the oxidation states of the dopant metal is less than 3^+ ; the amounts of the lithium extracted from the doped spinels decreases on increasing the dopant content. It shows a typical 4-V peak corresponding to the Mn^{4+}/Mn^{3+} couple [17]. As reported by Ozhuku et al. [7], the Ni-substituted LiMn₂O₄ system presents a single oxidation-reduction reaction above 4.5 V. However, the present system was cycled up to 4.2 V for the fear of decomposition of electrolyte. The prominent double peak observed in the Ni-doped is similar to that observed by others who studied Ni-doped LiMn₂O₄ [17]. This double peak is attributed to the progressive oxidation of Ni²⁺ to Ni⁴⁺ through Ni³⁺.

Fig. 5 depicts the discharge capacity, coluombic efficiency vs. cycle number. It is seen from the figure that the cells with spinel compound $LiNi_{0.01}Co_{0.01}Mn_{1.98}O_4$ exhibits higher capacity and coloumbic efficiency than with the spinel $LiNi_{0.1}Co_{0.1}Mn_{1.8}O_4$ for the cycling so far investigated. Generally, spinels with smaller lattice con-



Fig. 5. Capacity, coloumbic efficiency vs. cycle number of $LiNi_{0.01}$ $Co_{0.01}Mn_{1.98}O_4$ and $LiNi_{0.1}Co_{0.1}Mn_{1.8}O_4$ cells. (1) Coloumbic efficiency of $LiNi_{0.01}Co_{0.01}Mn_{1.98}O_4$; (2) discharge capacity of $LiNi_{0.01}Co_{0.01}Mn_{1.98}O_4$; (3) coloumbic efficiency of $LiNi_{0.1}Co_{0.1}Mn_{1.8}O_4$; (4) discharge capacity of $LiNi_{0.1}Co_{0.1}Mn_{1.8}O_4$.

stants show better cyclability. According to Amatucci et al. [18], LiAl_{0.1}Mn_{1.8}O₄ synthesized by a solid-state method in which the lattice parameter 'a' was 8.191 A° showed a much improved cyclability. In the present study, the spinel compound $\text{LiNi}_{0.01}\text{Co}_{0.01}\text{Mn}_{1.98}\text{O}_4$, which has the lattice of 8.221 A° , shows better cyclability than the other one. This decrease in lattice constant of multidoped spinel structure increases the concentration of Mn4+ ions in the spinel structure by substituting Mn³⁺ ions with the metal ions. High initial capacity and capacity retention are the two desirable properties of the cathode materials to achieve good battery performance. The cycling behavior of LiMn₂O₄ cells has been demonstrated by many researchers [3–8]. Hwang et al. [19] reported the charge–discharge profile undoped LiMn₂O₄. According to Hwang et al. [19], the initial capacity of the undoped LiMn₂O₄ decreases dramatically even after second cycle and loses about 30% of its initial capacity about 20 cycles. Also, the capacity retention has been found to be poor. In contrast, in the present study, the initial and the capacity retention of the cells after cycling were maintained because structure of the LiMn₂O₄ spinel is stabilized as the Co ions delivers high initial capacity and the Ni ions maintain good capacity retention [19].

In order to understand the various electrochemical processes taking place in the Li cells, the electrochemical impedance measurements have been made for both asassembled and fully charged states (4.2 V). Generally, Nyquist plots appear with one or two semicircles and a Warburg impedance associated with the diffusion of lithium ions with the passive layer on the electrode, whereas the second one is with the charge–transfer resistance coupled with the capacitance at the surface film/cathode particle interface arising from surface-adsorbed species. Figs. 6 and 7 show the Nyquist plots of the cells with LiNi_{0.01}



Fig. 6. Nyquist plots at different cell voltages: (a) V=2.7 and (b) V=4.2 for $\text{LiNi}_{0.01}\text{Co}_{0.01}\text{Mn}_{1.98}\text{O}_4$.

Co_{0.01}Mn_{1.98}O₄ and LiNi_{0.1}Co_{0.1}Mn_{1.8}O₄, respectively, at as-assembled and fully charged conditions. The electrolyte resistance "Re" will not depend on the voltage at which the impedance spectra is recorded because the electrolyte concentration remains invariant, and variation in the lithium content of the electrodes need not influence the electrolyte conductivity. For both the systems, the charge-transfer resistance is diminished in the charged state, which indicates the material becomes more conductive at the higher state of charge. The resistance of the fully charged cathode material is expected to be higher because when surface of the film grows, the charging voltage is raised. But in the present study, the pristine samples exhibited higher resistance. The reason for this increase in resistance is attributed as follows. According to Aurbach et al. [20], based on their FTIR studies, pristine LiCoO₂ and LiMn₂O₄ were covered with a layer of Li₂CO₃, formed by the interaction of the basic LiMOx oxide with the acidic CO_2 in the atmosphere. This



Fig. 7. Nyquist plots at different cell voltages: (a) V=2.7 and (b) V=4.2 for $LiNi_{0.1}Co_{0.1}Mn_{1.8}O_4$.

layer is a compact layer giving a high resistance. When the cells are charged, the electrodes become covered with a surface layer of RCOOLi due to interaction of the cathode material with the EC-DMC electrolyte [21]. At high charging voltages, the deintercalation processes is accompanied by changes in volume of the cathode and thickness of its surface layer. These changes together with the numerous by-pass channels formed for lithium migration could have reduced the resistance of the film at the cathode surface at charging voltages [22].

4. Conclusions

The compounds $LiNi_{0.01}Co_{0.01}Mn_{1.98}O_4$ and $LiNi_{0.1}Co_{0.01}Mn_{1.8}O_4$ were prepared through sol-gel method. $LiNi_{0.01}Co_{0.01}Mn_{1.98}O_4$ is found to be suitable for lithium battery applications considering discharge capacity and coloumbic efficiency.

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