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Electrochemical performance behavior of combustion-synthesized $LiNi_{0.5}Mn_{0.5}O_2$ lithium-intercalation cathodes

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Abstract

$LiNiO_2$, partially substituted with manganese in the form of a $LiNi_{0.5}Mn_{0.5}O_2$ compound, has been synthesized by a gelatin assisted combustion method [GAC] method. Highly crystalline $LiNi_{0.5}Mn_{0.5}O_2$ powders with *R3m* symmetry have been obtained at an optimum temperature of 850 °C, as confirmed by PXRD studies. The presence of cathodic and anodic CV peaks exhibited by the $LiNi_{0.5}Mn_{0.5}O_2$ cathode at 4.4 and 4.3 V revealed the existence of Ni and Mn in their 2+ and 4+ oxidation states, respectively. The synthesized $LiNi_{0.5}Mn_{0.5}O_2$ cathode has been subjected to systematic electrochemical performance evaluation, via capacity tapping at different cut-off voltage limits (3.0–4.2, 3.0–4.4 and 3.0–4.6 V) and the possible extraction of deliverable capacity under different current drains (0.1*C*, 0.5*C*, 0.75*C* and 1*C* rates). The $LiNi_{0.5}Mn_{0.5}O_2$ cathode exhibited a maximum discharge capacity of 174 mAh g^{-1} at the 0.1*C* rate between 3.0 and 4.6 V. However, a slightly decreased capacity of 138 mAh g^{-1} has been obtained in the 3.0–4.4 V range, when discharged at the 1*C* rate. On the other hand, extended cycling at the 0.1*C* rate encountered an acceptable capacity fade in the 3.0–4.4 V range (<10%) for up to 50 cycles.

Keywords: Combustion synthesis; $LiNi_{0.5}Mn_{0.5}O_2$ cathode; Specific capacity; Cyclic voltammetry

1. Introduction

Ever since the commercialization of lithium-ion technology, lithium cobalt oxide has been widely used as a cathode active material due to its advantages of easy preparation, high voltage, good reversibility and high theoretical specific capacity [1]. However, due to the unavoidable shortcomings of $LiCoO_2$ such as structural instability at lower lithium content [2], safety [3], toxicity, high cost nature, etc., much effort has been made to develop cheaper and comparably performing cathode materials in place of $LiCoO_2$. To this end, $LiNiO_2$ and $LiMnO_2$ have been studied extensively as possible alternatives to $LiCoO_2$ [4–6].

Among the two alternate cathode candidates, layered $LiNiO_2$ possesses several advantages that include non-toxicity, inherent high capacity, possibility of allowing higher lithium extraction for a fixed cut-off voltage, lower intercalation potential (compared to that of $LiCoO_2$), etc. But difficulties involved in the synthesis of a stoichiometric $LiNiO_2$ compound and the larger capacity decay during prolonged cycling are the major constraints so that studies on partially substituted $LiNiO_2$ cathodes have gained importance in recent research. Several research groups have investigated the synthesis of the $LiNi_{0.5}Mn_{0.5}O_2$ cathode material in view of its comparable performance to $LiCoO_2$ along with better thermal stability [7,8]. Ohzuku and Lu et al. [8,9] have reported a 1:1 solid solution of $LiNiO_2$ and $LiMnO_2$ by employing solid-state synthesis, thus eliminating the drawbacks of capacity fading and structural instability. Also, few other researchers [10,11] have reported the synthesis of layered $LiNi_{0.5}Mn_{0.5}O_2$ cathode material and suggested that either high temperature calcination above 900 °C or longer dwelling times are required to prepare a phase-pure $LiNi_{0.5}Mn_{0.5}O_2$ cathode.

A simple gelatin assisted combustion [GAC] method is used in the present work to prepare $LiNi_{0.5}Mn_{0.5}O_2$ cathode material with the combination of preferred physical and electrochemical properties. The GAC method involves a single-step process with good product yield, relatively short processing time at moderate temperature, high chemical homogeneity and mono dispersed particles which contribute to good electrochemical

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performance. Although a wide variety of lithium battery electrodes have already been synthesized and demonstrated [12–14] with use of different combustible fuels for better electrochemical performance, a newer attempt to explore the possibility of using gelatin as the combustible fuel and the deployment of the GAC method to synthesize the title compound with preferred battery active characteristics is the subject of the present study. The structure and electrochemical properties of the powders were investigated by XRD, cyclic voltammetry and charge discharge studies for better understanding of the synthesized $LiNi_{0.5}Mn_{0.5}O_2$ compound against lithium metal.

2. Experimental

A soft chemistry route based on the nitrate-combustion method has been adopted [15] to synthesize a $LiNi_{0.5}Mn_{0.5}O_2$ compound using nitrate precursors and gelatin as the combustible component (to aid the process of combustion). Stoichiometric amounts of lithium nitrate, nickel nitrate and manganese nitrate (1:1:1 wt%) were dissolved in doubly distilled water to get a clear solution. To this solution was added a well stirred solution of gelatin in water and the resultant homogenous solution was heated initially at 90–100 °C for 1 h to obtain a viscous solution. The viscous solution thus obtained was dried at 120 °C for 12 h and subjected to different calcination temperatures: 200, 400, 600 and 850 °C for 3 h individually. Heat treatments at various temperatures were carried out mainly to understand the effect of the calcination temperature upon synthesizing a phase-pure compound and to identify the optimum temperature required to synthesize a better performing $LiNi_{0.5}Mn_{0.5}O_2$ compound. The ultra fine powders obtained at the end of the final calcination process were collected and subjected to characterization studies.

The phase purity of the product was verified using a Philips X-ray diffractometer. XRD patterns were recorded using nickel-filtered Cu Kα radiation at room temperature in the 2θ ranges 10–70° at a scan rate of $0.02^\circ\ s^{-1}$. Cyclic voltammetry and charge discharge studies were carried out with crimp sealed 2016 coin cells. Lithium metal was used as the anode and 1 M $LiPF_6$ in ethylene carbonate (EC):dimethyl carbonate (DMC) as the electrolyte. The cathode was prepared by mixing 88% active material with 5% super-P carbon and 7% poly(vinylidene fluoride) (PVdF) binder in *N*-methyl-2-pyrrolidone (NMP), which was coated on an aluminium foil and dried at 120 °C for 3 h in an oven. The resulting $LiNi_{0.5}Mn_{0.5}O_2$ coating on aluminium foil was roll-pressed and the electrode was punched out to the required dimension with a punching machine. 2016 coin cells were assembled in a glove box and cycled at different cut-off voltages and at different discharge rates using a Toyo multi channel battery cycle life tester.

3. Results and discussion

3.1. XRD analysis

X-ray diffraction patterns recorded for $LiNi_{0.5}Mn_{0.5}O_2$ powders heated at 200, 400, 600 and 850 °C for 3 h, respectively, are shown in Fig. 1a–d. It is evident from Fig. 1 that some undesirable additional peaks were obtained between 20° and 40° (2 theta values) for the samples heated at 200 and 400 °C. The presence of such peaks may be attributed to the co-existence of trace impurities such as $LiNO_3$, Li_2CO_3 and NiO [16,17] along with $LiNi_{0.5}Mn_{0.5}O_2$ compound. On the other hand, the XRD pattern of the $LiNi_{0.5}Mn_{0.5}O_2$ compound synthesized at 600 °C shows the presence of characteristic peaks in the respective positions, but with lower intensity. This is an indication that the process of crystallization has started at 600 °C and the same needs to be completed at a slightly higher temperature to get single phase product with good crystallinity. In other words, it is understood that further calcination at a higher temperature is essential to obtain the $LiNi_{0.5}Mn_{0.5}O_2$ compound with high purity and crystallinity, despite some compound formation at lower temperature. As expected, the compound synthesized at 850 °C exhibited a well defined diffractogram that contains sharp and highly intense peaks. Incidentally, the intensities of the (0 0 3) reflections are higher than (1 0 4) reflections, which is an indication that the compound has good cation ordering [18,19]. Similarly, hexagonal doublets such as (0 0 6/1 0 2) and (1 0 8/1 1 0) are seen with clear splitting, which confirms that the synthesized $LiNi_{0.5}Mn_{0.5}O_2$ compound has a high degree of crystallinity, good hexagonal ordering and better layered characteristics [20]. Thus, the newly adopted GAC method has been found to be advantageous over the conventional solid state or mixed hydroxide method [21] in preparing highly ordered $LiNi_{0.5}Mn_{0.5}O_2$ powders of ultra fine nature.

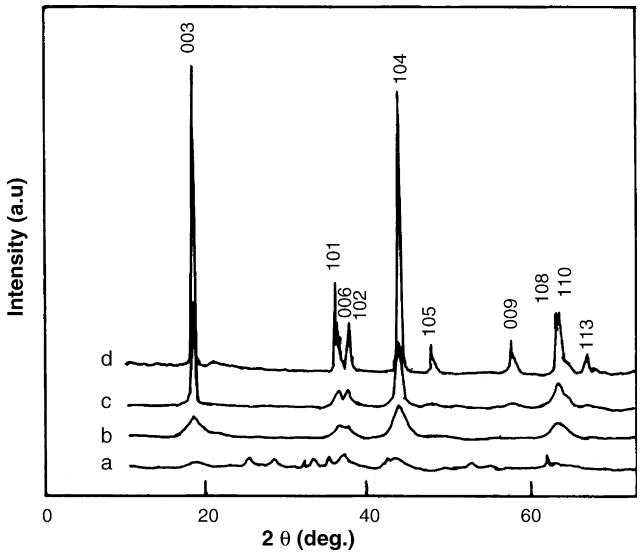

Fig. 1. XRD patterns of $LiNi_{0.5}Mn_{0.5}O_2$ powder synthesized at: (a) 200 °C, (b) 400 °C, (c) 600 °C and (d) 850 °C.

The recorded XRD pattern when indexed to an α-$NaFeO_2$ type structure with a *R*3*m* space group showed perfect fitting of the peaks. The calculated hexagonal lattice parameters of the compound $LiNi_{0.5}Mn_{0.5}O_2$ (synthesized at 850 °C) obtained by the least squares fitting of the *h k l* and two values are: $a = 2.890$ Å and $c = 14.298$ Å. These values closely agree with the literature values reported by Ohzuku and Makimura ($a = 2.892$ Å and $c = 14.301$ Å) [7] and Lu et al. ($a = 2.890$ Å

and $c = 14.296$ Å) [21]. However, the lattice parameter values of the $LiNi_{0.5}Mn_{0.5}O_2$ compound synthesized at lower (400 °C) and moderate temperatures (600 °C) differ considerably from the reported values. Based on this observation, it is deduced that a temperature of 850 °C is essential to synthesize the $LiNi_{0.5}Mn_{0.5}O_2$ compound with the preferred physical characteristics. Further, the integrated intensity ratio of the (0 0 3) to (1 0 4) lines of $LiNi_{0.5}Mn_{0.5}O_2$ synthesized at 850 °C is 0.97 and the same is also in agreement with the values reported by Ohzuku and Makimura (0.84) [7] and Lu et al. (∼1.0) [21]. This is an indication that there may be a fractional and not a significant cation mixing in the synthesized cathode, wherein part of Ni and Li ions may undergo interchange of sites in the crystal lattice. However, based on the observed $I_{(0\,0\,3)}/I_{(1\,0\,4)}$ value, it is believed that the fractional cation mixing may not lead to the formation of inactive rock-salt domains that affects the electrochemical property [7].

Hence, based on the PXRD observations, it can be concluded that the optimum temperature required for complete hexagonal ordering of $LiNi_{0.5}Mn_{0.5}O_2$ compound is 850 °C. So, further electrochemical characterization studies such as cyclic voltammetry and charge–discharge were carried out for $LiNi_{0.5}Mn_{0.5}O_2$ compound synthesized at 850 °C only.

3.2. Cyclic voltammetry studies

Cyclic voltammetry is a useful technique to evaluate the cycling performance of the $LiNi_{0.5}Mn_{0.5}O_2$ electrode, which has a potential range of 2.5–5.0 V versus Li/Li^+ with Li metal as the reference and counter electrode. The scan rate was fixed as 50 μV s^{-1}. The cyclic voltammogram for $LiNi_{0.5}Mn_{0.5}O_2$ synthesized at 850 °C for 12 h, in 1 M $LiPF_6$ in EC/DMC (1:1), is given in Fig. 2. Two anodic peaks corresponding to the de-intercalation of Li^+ are observed at 4.1 and 4.4 V and two more cathodic peaks at about 3.75 and 4.3 V. Such peaks produced by the $LiNi_{0.5}Mn_{0.5}O_2$ cathode are entirely different from those of the parent $LiNiO_2$ which exhibits three sharp anodic and cathodic peaks that are normally attributed to phase changes such as hexagonal to monoclinic, monoclinic to hexagonal and hexagonal to hexagonal in $LiNiO_2$ [22]. It was already reported that the presence of sharp peaks near 3 V region is found to get diminished gradually by 20% in the $LiNi_{0.8}Co_{0.2}O_2$ compound [23], when cobalt is partially substituted in the $LiNiO_2$ matrix. Similarly, in the present study also, oxidation and reduction peaks are not observed in the 3 V region, which is clear from Fig. 2. Hence, it is confirmed that the partially substituted Mn has successfully been incorporated into the $LiNiO_2$ matrix, as implied already from the PXRD studies. Also, it is further understood that the GAC method could be employed effectively to synthesize a $LiNi_{0.8}Co_{0.2}O_2$ solid solution with good electrochemical characteristics.

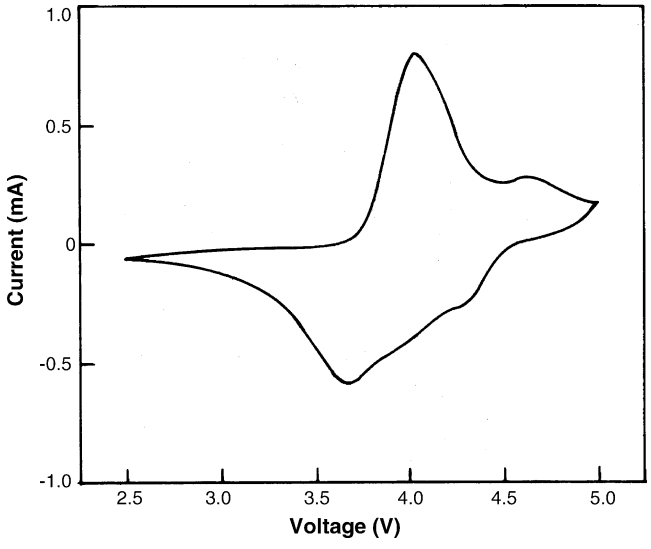

Fig. 2. Cyclic voltammogram exhibited by the $Li/LiNi_{0.5}Mn_{0.5}O_2$ cell.

Paulsen et al. [24] reported that the $Mn^{3+} \leftrightarrow Mn^{4+}$ redox reaction occurs at about 2.9 V versus Li/Li^+ in the layer-structured $Li_{2/3}(Ni_{1/3}Mn_{2/3})O_2$. However, the absence of such redox peaks in the 3 V region of $LiNi_{0.5}Mn_{0.5}O_2$ cathode indicates that Mn ions are not in the 3+ oxidation state; rather they may presumably be in the electrochemically inactive form of 4+ oxidation state [25]. Similarly, the presence of respective major anodic and cathodic peaks at 4.1 and 3.75 V may be ascribed to the $Ni^{2+} \leftrightarrow Ni^{4+}$ redox reaction. This observation is similar to the presence of the $Ni^{2+/4+}$ couple observed in the $xLi(Ni_{0.5}Mn_{0.5})O_2 \cdot (1-x)Li_2TiO_3$ compound reported by Kim et al. [26] and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ systems by Shaju et al. [27]. Hence, peaks at 4.1 and 3.75 V may be attributed to the redox reactions of either the Ni^{2+}/Ni^{3+} or the Ni^{2+}/Ni^{4+} couple. Similarly, the presence of such peaks at the respective positions is an indication of the presence of a single phase layered compound, as reported by Kang et al. [28] and Lu et al. [21]. On the other hand, the anodic and cathodic shoulder peaks that are seen, respectively, at 4.4 and 4.3 V (Fig. 2) may be assigned to the presence of Ni and Mn ions are in their 2+ and 4+ oxidation states, respectively [29], because such existence of $Ni^{2+} + Mn^{4+}$ alone can lead to a possible valence-degeneracy to a smaller extent, based on the $Ni^{2+} + Mn^{4+} \leftrightarrow Ni^{3+} + Mn^{3+}$ ion equilibrium. Hence, it is understood that the reversible shoulder peak observed at 4.4–4.5 V for the anodic and 4.20–4.35 V in the cathodic scans of CV are indications of participation of the $Ni^{2+/3+}$ and $Mn^{4+/3+}$ couple in the synthesized $LiNi_{0.5}Mn_{0.5}O_2$ cathode.

3.3. Charge–discharge characteristics

Charge–discharge characteristics of the $Li/LiNi_{0.5}Mn_{0.5}O_2$ cells were studied at different voltage ranges from 3.0 to 4.2, 4.4 and 4.6 V at 0.1C rate and the observed discharge behavior is reported in Fig. 3a. Similarly, variation of specific discharge capacity values with respect to different discharge rates (0.1C, 0.5C, 0.75C and 1C rate) in the 3.0–4.4 V region was studied for $Li/LiNi_{0.5}Mn_{0.5}O_2$ and the results are depicted in Fig. 3b.

Basically, an initial charging capacity [Q_c] of ∼190 mAh g^{-1} was observed for all the three cut-off voltages and the corresponding discharge capacity [Q_d] values for the 4.2, 4.4 and 4.6 V cut-off range were 146, 158 and 174 mAh g^{-1}, respectively (Fig. 3a). Therefore, an initial capacity loss of about 16 mAh g^{-1} has been observed with respect to 3–4.6 V domain,

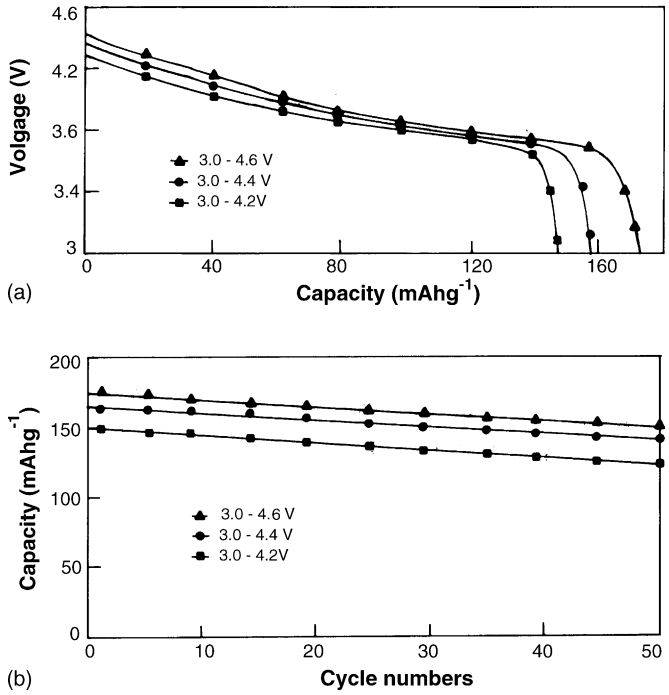

Fig. 3. (a) Discharge curves obtained galvanostatically at the 0.1*C* rate in the range: 3.0–4.2, 3.0–4.4 and 3.0–4.6 V for a Li/$LiNi_{0.5}Mn_{0.5}O_2$ cell. (b) Variation of capacity with cycle number for the Li/$LiNi_{0.5}Mn_{0.5}O_2$ cell (0.1 mA cm^{-2}) observed between 3.0 and 4.2, 3.0 and 4.4 and 3.0 and 4.6 V.

and a loss of about 32 and 44 mAh g^{-1} has been exhibited in the 3–4.4 and 3–4.2 V voltage domains, respectively. So, the upper cut-off voltage [4.6 V] is found to reduce the initial irreversible capacity loss significantly compared to the 4.2 and 4.4 V regions. In other words, the initial columbic efficiency was found to improve from 77% [3–4.2 V] to 92% [3–4.6 V], when the charging cut-off voltage was increased from 4.2 to 4.6 V.

Based on the high initial charge (190 mAh g^{-1}) and lower discharge capacity (146 mAh g^{-1}) values exhibited by $LiNi_{0.5}Mn_{0.5}O_2$ cathode in the 3.0–4.2 V limit, the involvement of the $Ni^{2+/4+}$ couple [30] is also expected to play a vital role in the charge–discharge process. In other words, the encountered capacity loss of 44 mAh g^{-1} reveals that full re-insertion of the extracted Li is not possible. This could be due to a fractional cation mixing (Ni^{2+} occupying Li^+ site and vice versa) in the compound. Generally, the size proximity of Ni^{2+} (ionic radius, $r_{Ni^{2+}} = 0.69$ Å) and Li^+ ($r_{Li^+} = 0.76$ Å) [31] ions allows easy interchange of them in the inter slab and enhances the chance for cation mixing [31,32]. Upon successive removal of Li around the Ni^{2+} in the Li-layer, a collapse of the inter slab space would result, due to the oxidation of Ni^{2+} to Ni^{3+}, which would limit the re-insertion of Li during the subsequent discharge process [33,34]. As a result, considerable irreversible capacity loss would become deliberately unavoidable. Thus, the higher initial capacity fade observed with the 3–4.2 V range in $LiNi_{0.5}Mn_{0.5}O_2$ cathode could be understood. However, this has been reduced to an acceptable level of < 18%, when charged to 4.4 and 4.6 V, which is the advantage of the charging of the $LiNi_{0.5}Mn_{0.5}O_2$ cathode to higher voltages and the significance of the GAC method to synthesize such a well-performing cathode material in the higher voltage regions. This is further substantiated by the fact that the magnitudes of the specific capacity values (~170 mAh g^{-1}) exhibited by $LiNi_{0.5}Mn_{0.5}O_2$, synthesized by the GAC method, are found to be either comparable or better than those exhibited by the compound synthesized with other methods [35–37].

Upon subsequent cycling, only a small decrease in the Q_d values such as 146–140 mAh g^{-1} (3.0–4.2 V), 158–152 mAh g^{-1} (3.0–4.4 V) and 174–170 mAh g^{-1} (3.0–4.6 V) were observed, as evident from Fig. 3b. In other words, the magnitude of the coulombic efficiency was found to improve linearly upon cycling, especially with respect to higher cut-off voltages. Ultimately, the coulombic efficiency of $LiNi_{0.5}Mn_{0.5}O_2$ cathode has been improved significantly from the first cycle (78–90%) and the same has been maintained (≥95%) upon progressive cycling in the present investigation. Such an interesting observation is an indication that the title compound has a good storage capacity to qualify as a potential lithium battery cathode material. Thus, the newly adopted GAC method has played a important role in minimizing cation mixing, enhancing coulombic efficiency and maintaining the structural stability of the $LiNi_{0.5}Mn_{0.5}O_2$ cathode upon cycling.

Fig. 4 shows the results of rate capability tests performed on a Li/$LiNi_{0.5}Mn_{0.5}O_2$ cell. The cells were discharged at different rates viz., 0.1*C*, 0.5*C*, 0.75*C* and 1*C*, in the voltage range 3.0–4.4 V, and indicated slightly decreased capacity and coulombic efficiency values with increasing discharge rates. It is evident from Fig. 4 that an initial discharge capacity value of 158 mAh g^{-1} has been observed when cycled at 0.1*C* rate, followed by slightly decreased values such as 150, 145 and 138 mAh g^{-1} with 0.5*C*, 0.75*C* and 1*C* rates, respectively. The small variation or decrease in the observed discharge capacity values with the increasing discharge rates may presumably be due to the increased impedance of the electrode that relates to the reactions of the electrolytic solvents and cathode material or to the oxidative decomposition of electrolyte solvents on the surface of the cathode material. However, the specific capacity of Li/$LiNi_{0.5}Mn_{0.5}O_2$ cells exhibited at the end of 50 cycles was found to be more than 150, 138 and 120 mAh g^{-1} with respect to the 0.5*C*, 0.75*C* and 1*C* discharge rates, which is a satisfactory cycling performance of the synthesized $LiNi_{0.5}Mn_{0.5}O_2$ cathode. So, a nominal and an acceptable capacity loss of ~10% has been observed when cycled at the 1*C* rate, whereas an

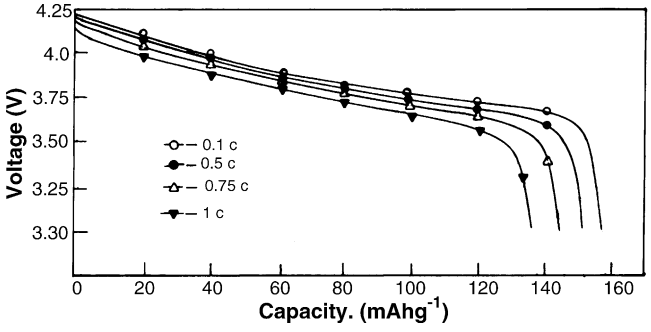

Fig. 4. Discharge curves exhibited by a Li/$LiNi_{0.5}Mn_{0.5}O_2$ cell discharged galvanostatically at different rates, viz., 0.1*C*, 0.5*C*, 0.75*C* and 1*C*.

excellent capacity retention ($\leq$5%) has been exhibited by the Li/$LiNi_{0.5}Mn_{0.5}O_2$ cells upon progressive cycling when discharged at the 0.5*C* and 0.75*C* rates.

4. Conclusion

A layered $LiNi_{0.5}Mn_{0.5}O_2$ compound with excellent homogeneity and crystallinity has been synthesized by adopting a gelatin assisted combustion method at 850 °C. Based on XRD observations, the optimum temperature required to synthesize a phase-pure and better performing $LiNi_{0.5}Mn_{0.5}O_2$ compound has been identified as 850 °C, since the sample synthesized at 850 °C is found to be highly crystalline with the reported lattice parameter values. The stable existence and the cycling behavior of the synthesized $LiNi_{0.5}Mn_{0.5}O_2$ solid solution with Ni^{2+} and Mn^{4+} is very well established from the CV studies. Li/$LiNi_{0.5}Mn_{0.5}O_2$ cells delivered a specific capacity of 174 mAh g^{-1} at the 0.1*C* rate between 3.0 and 4.6 V at room temperature with about a 90% coulombic efficiency. However, slightly decreased discharge capacity values with enhanced coulombic efficiency (90–96%) have been observed at higher discharge rates (0.5–1*C* rate). Interestingly, no significant capacity loss has been observed upon extended cycling, especially when cycled at the 0.1*C* rate. Thus, the compound $LiNi_{0.5}Mn_{0.5}O_2$ synthesized via GAC method may be considered favorably for practical lithium battery applications, since it possesses good energy-storing capability and better cycleabilty.

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