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Synthesis and electrochemical characterization of 4 V $LiR_XMn_{2-X}O_4$ spinels for rechargeable lithium batteries

Gopu Kumar [a,*], H. Schlorb [b], D. Rahner [b]

[a] Lithium Battery Division, Central Electrochemical Research Institute (CSIR), Karaikudi 630006, Tamilnadu, India

[b] Dresden Institute of Technology, Institut fur Physikalische und Elektrochemie, Dresden, Germany

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Abstract

Lithium ion cells have attracted the researchers ever since the first commercialization of $Li//LiCoO_2$ cells in Japan. However, the high cost and relatively low availability of cobalt has promoted the search for inexpensive and widely available manganate materials. $LiMn_2O_4$ is one of these materials which is being investigated extensively. However, $LiMn_2O_4$ shows fading of capacity during cycling involving mainly the Jahn–Teller Mn^{3+} ion. In the present work, $LiR_XMn_{2-X}O_4$ (R=Co, Ni, Fe, Ti) spinel compounds have been synthesized using low and high temperature methods. These materials were structurally evaluated using XRD. The prepared materials were electrochemically investigated using cyclic voltammetry and galvanostatic cycling techniques. The best performing material was assembled in a coin cell of type 2032 and charged at 500 μA up to 4.4 V. The cells were cycled at 1 mA current drain using 1 M $LiClO_4$/PC as an electrolyte. The results indicate that Ti doped spinel shows promising results. Electrical characteristics of these cells are presented in this paper.

Keywords: Doped lithium manganese oxide; Cyclic voltammetry; Galvanostatic cycling; Lithium battery

1. Introduction

Lithium is an attractive metal with very positive characteristics like very low electrode potential, high electrochemical equivalence, low equivalent weight, etc. Due to these properties, lithium is highly attractive for use as negative electrode in energy storage systems [1].

Primary lithium batteries have dominated the area of battery development for the past three decades due to their high energy density, cell voltage, wide temperature range of operation, long shelf-life, etc. Majority of this work [2] in the area of primary lithium batteries was concentrated on using MnO_2 as a cathode material. Efforts were made to develop secondary lithium batteries in 1980 using traditional cathode materials like MnO_2, MoS_2, TiS_2 and others. However, the low cyclability and the pronounced dendritic growth of lithium metal coupled with safety problems made realization of such systems rather difficult [3]. Sustained efforts by several researchers led to the idea of dual intercalation electrodes (anode, cathode) for fabricating safer and more reliable rechargeable lithium ion batteries [4–7].

Rocking chair or swing batteries are one of the most recent developments in the area of energy storage systems. The technology involves the use of lithiated transition metal oxide cathodes, an intercalating carbon anode in a suitable non-aqueous electrolyte medium. Various transition metal oxides like $LiMn_2O_4$, $LiCoO_2$, $LiNiVO_4$ have been investigated by several workers [8–14] for use as positive electrodes in lithium ion cells. Among these materials, the lithium manganese spinel ($LiMn_2O_4$) is attractive in view of its various advantages like low cost, ease of synthesis, non-toxicity, etc. [11]. However, $LiMn_2O_4$ suffers from capacity fade which limits cyclability [12]. In order to have good cyclability with marginal sacrifice of capacity, several attempts [14–17] have been made for synthesizing improved lithium manganese spinels doped with various metals like Al, Mg, Co, Cr, etc.

In this paper we present a comprehensive investigation on the electrochemical characterization of lithium manganese spinels doped with metals like Co, Ni, Fe, Ti synthesized at low as well as at high temperatures. Based on the electrochemical performance of the doped lithium manganese spinels, promising materials were selected, assembled in coin type cells (2032) and investigated.

2. Experimental

$LiMn_2O_4$ (Merck, Germany) was used as a reference material. Low temperature synthesis of $LiMn_2O_4$ doped with

* Corresponding author.
E-mail address: gkumar41@hotmail.com (G. Kumar).

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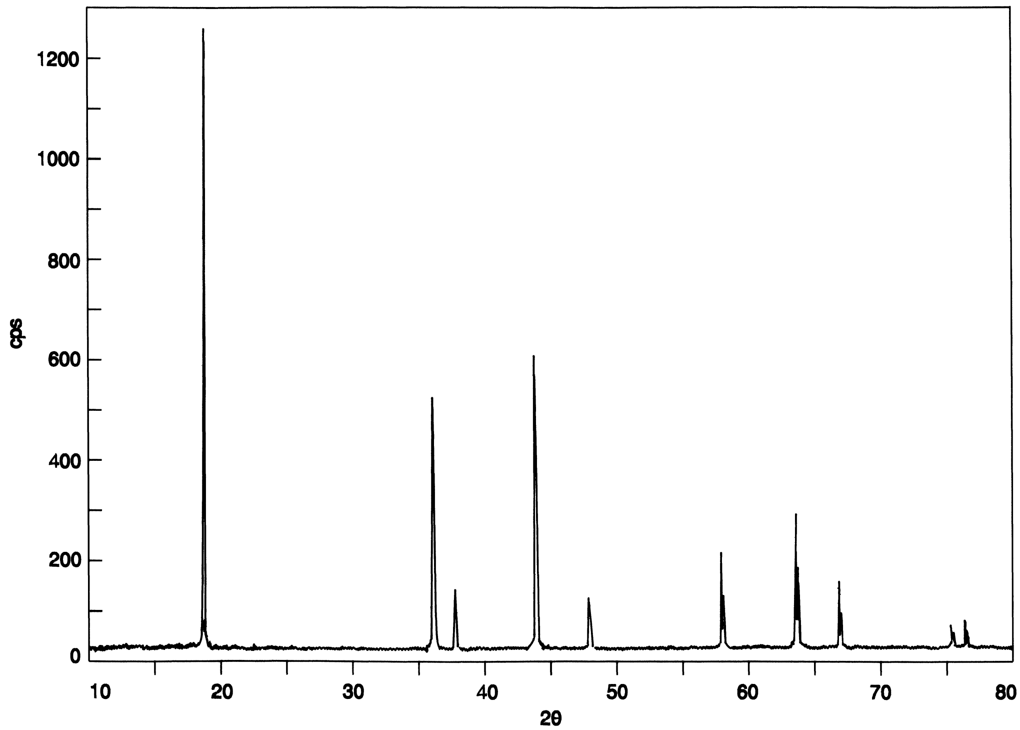

Fig. 1. X-ray diffraction of synthesized $LiTi_{0.05}Mn_{1.95}O_4$.

Co, Ni, Fe was carried out using the respective formate precursors vacuum dried at 400°C. X-ray diffractometry (XRD) was carried out using Cu Kα radiation. Proper care was taken for any possible side reaction with moisture.

High temperature doped (Co, Ni, Fe) lithium manganese spinels were obtained by firing the respective powders synthesized at low temperature up to 800–850°C for 72 h. Their phase purity and lattice parameters were

Table 1
Lattice constant of different spinels synthesized at high temperature

Compound	*a* (Å)
$LiMn_2O_4$	8.241
$LiFe_{0.05}Mn_{1.95}O_4$	8.234
$LiTi_{0.05}Mn_{1.95}O_4$	8.250
$LiCo_{0.05}Mn_{1.95}O_4$	8.247
$LiNi_{0.05}Mn_{1.95}O_4$	8.243

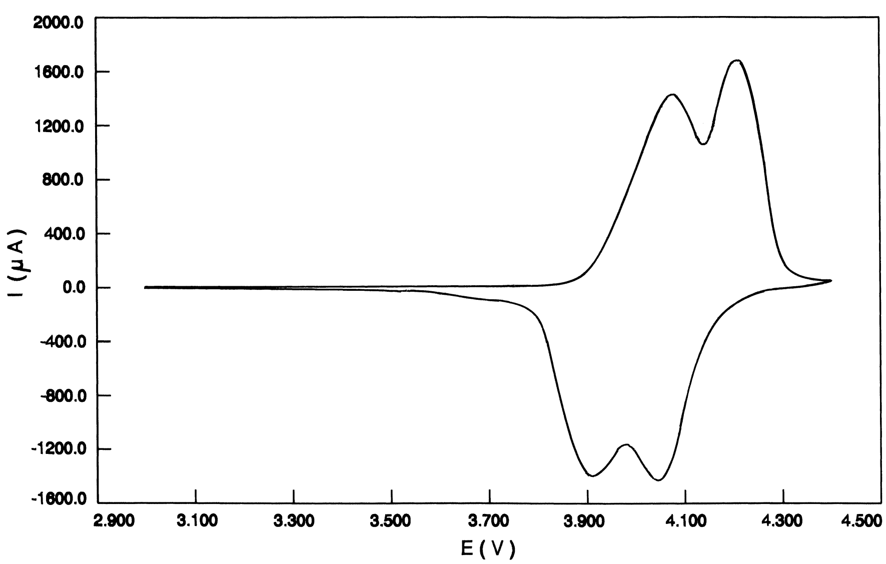

Fig. 2. Cyclic voltammogram of $LiMn_2O_4$.

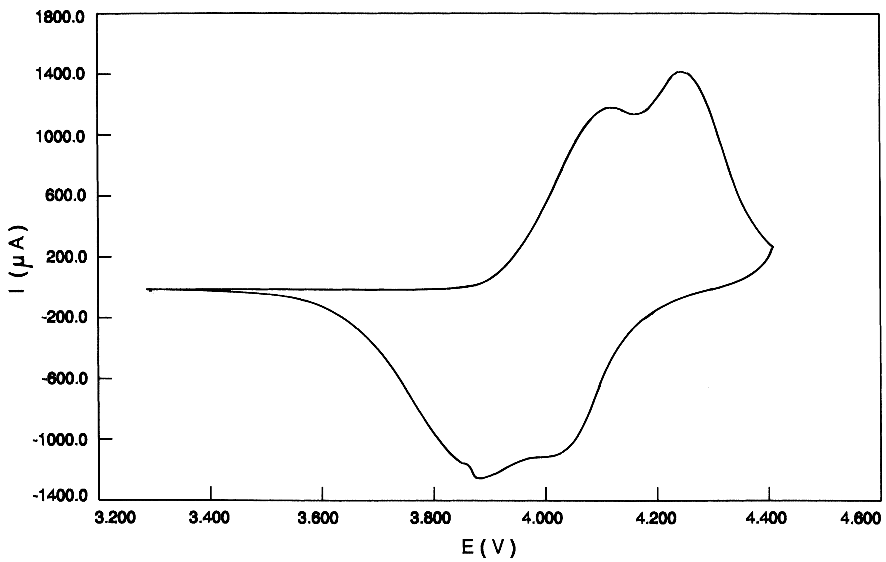

Fig. 3. Cyclic voltammogram of $LiTi_{0.05}Mn_{1.95}O_4$.

Table 2
Capacity ($mAh\,g^{-1}$) of different low temperature synthesized $LiMn_2O_4$ doped spinels obtained by cyclic voltammetry (CV) and galvanostatic cycling

Technique	Material[a]/capacity ($mAh\,g^{-1}$)						
	LM	$LC_{0.05}$	$LC_{0.5}$	$LN_{0.05}$	$LN_{0.5}$	$LF_{0.05}$	$LF_{0.5}$
Charge							
CV	70	72	35	72	10	71	46
Cycling		67	35	59	13	77	54
Discharge							
CV		60	29	59	11	62	38
Cycling		63	33	49	12	61	36

[a] LM: $LiMn_2O_4$; $LN_{0.5}$: $LiNi_{0.5}Mn_{1.5}O_4$; $LC_{0.05}$: $LiCo_{0.05}Mn_{1.95}O_4$; $LF_{0.05}$: $LiFe_{0.05}Mn_{1.95}O_4$; $LC_{0.5}$: $LiCo_{0.5}Mn_{1.5}O_4$; $LF_{0.5}$: $LiFe_{0.5}Mn_{1.5}O_4$; $LN_{0.05}$: $LiNi_{0.05}Mn_{1.95}O_4$.

evaluated using XRD technique. Titanium doped lithium manganese spinel was synthesized using stoichiometric amounts of Li_2CO_3, MnO_2 and TiO_2. The powder was heated initially to 450°C and finally fired at 850°C for 48 h. The sample was identified for phase purity using XRD technique.

Cyclic voltammetry and galvanostatic cycling studies of the above spinel materials were carried out using a three-electrode glass cell assembly. Lithium foil was used as reference as well as counter electrode and 1 M $LiClO_4$ in propylene carbonate (PC) as the electrolyte. All studies were carried out using a PAR 273A (EG&G Company) potentiostat with computerized interface. The glass cells were assembled in a glove box using argon atmosphere. All cyclic voltammetry experiments were carried out in the potential range 2.8–4.4 V at a scan rate of $50\,\mu V\,s^{-1}$. Similarly, galvanostatic cycling was also carried out in the potential range 2.5 to 4.4 V in 1 M $LiClO_4$/PC as electrolyte using a computer controlled cycle life tester (Digatron Company, Germany). Coin cells of type 2032 size were fabricated using lithium foil as the anode, spinel powder mixed with 10% teflonized acetylene black as the cathode, 1 M $LiClO_4$/PC as the electrolyte and Celgard 3050 as the separator. Pressed type cathodes were used and each pellet had an active mass of 270 mg. A nickel mesh was used as the current collector.

Table 3
Capacities of various doped $LiMn_2O_4$ spinels synthesized at high temperature obtained by cyclic voltammetry (CV) and galvanostatic cycling

Technique	Material[a]/capacity ($mAh\,g^{-1}$)					
	LM_c	$LC_{0.05}$	$LN_{0.05}$	$LF_{0.05}$	$LT_{0.05}$	$LT_{0.5}$
Charge						
CV	126	94	98	111	122	83
Cycling	106	97	96	110	119	80
Discharge						
CV	116	90	97	120	107	36
Cycling	103	93	96	111	97	37

[a] LM_c: $LiMn_2O_4$; $LT_{0.5}$: $LiTi_{0.5}Mn_{1.5}O_4$; $LT_{0.05}$: $LiTi_{0.05}Mn_{1.95}O_4$.

Table 4
Electrical characteristics of 4 V lithium coin cells

Parameters	Li//$LiMn_2O_4$	Li//$LiTi_{0.05}Mn_{1.95}O_4$
Cell type	2032	2032
Cell weight (g)	2.71	2.71
OCV (V)	4.13	4.16
Rated cell capacity ($mAh\,g^{-1}$)	35	35
Current drain (mA)	1	1
Energy density ($Wh\,kg^{-1}$)	175	180
Cycles	3	3
Temperature (°C)	−30 to +80	−30 to +80

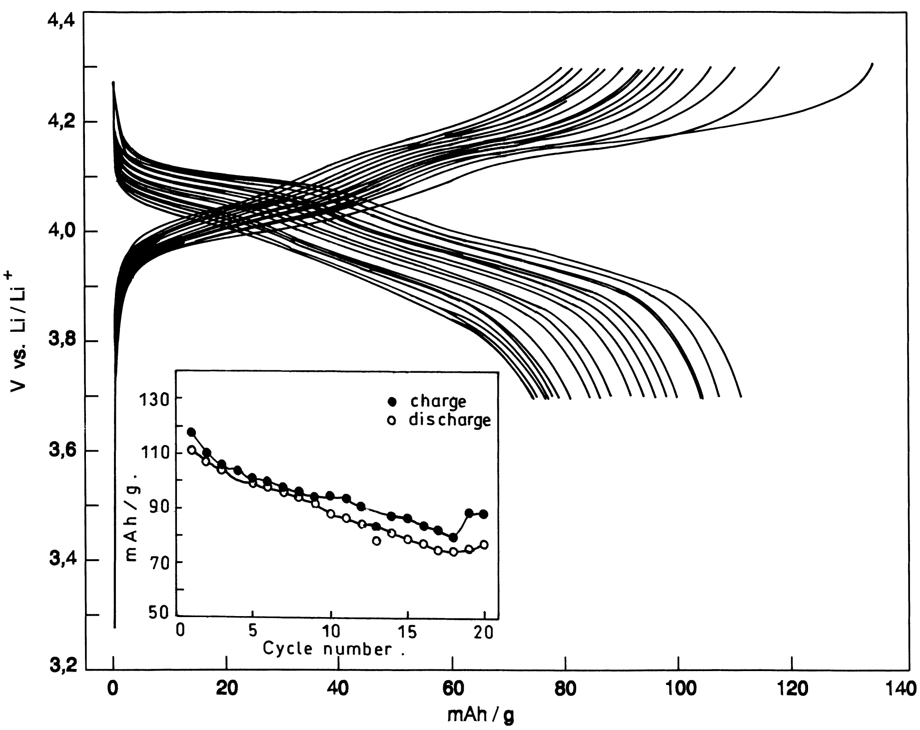

Fig. 4. Cycling behaviour of $LiTi_{0.05}Mn_{1.95}O_4$.

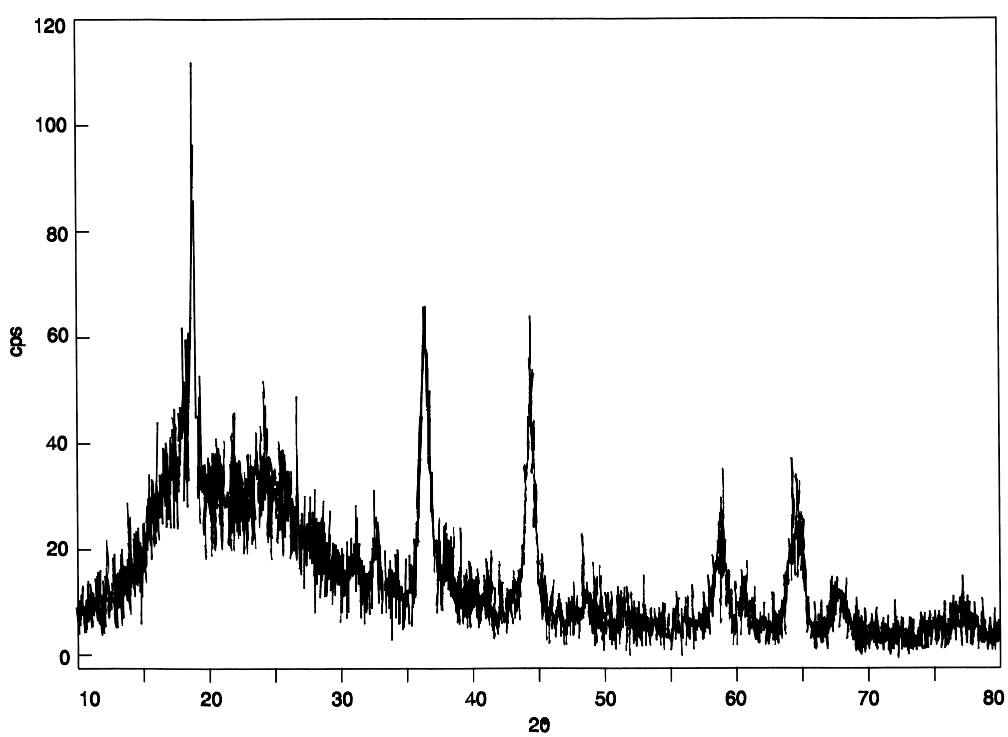

Fig. 5. X-ray diffraction of cycled $LiTi_{0.05}Mn_{1.95}O_4$.

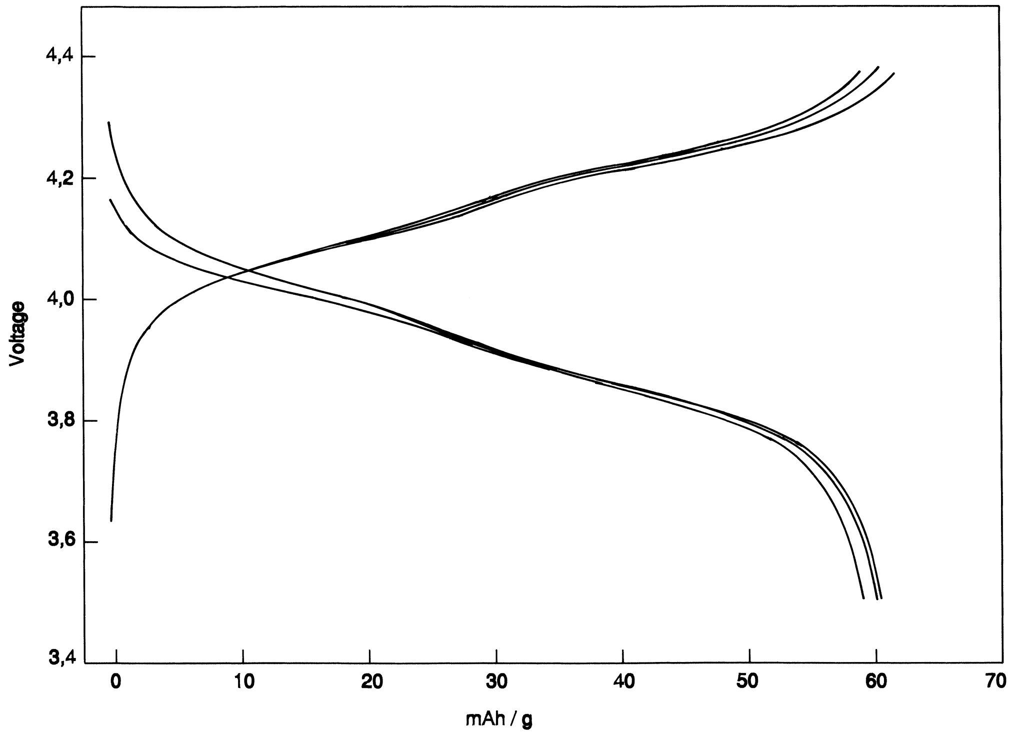

Fig. 6. Cycling behavior of $LiMn_2O_4$ (synthesized at low temperature) coin cell.

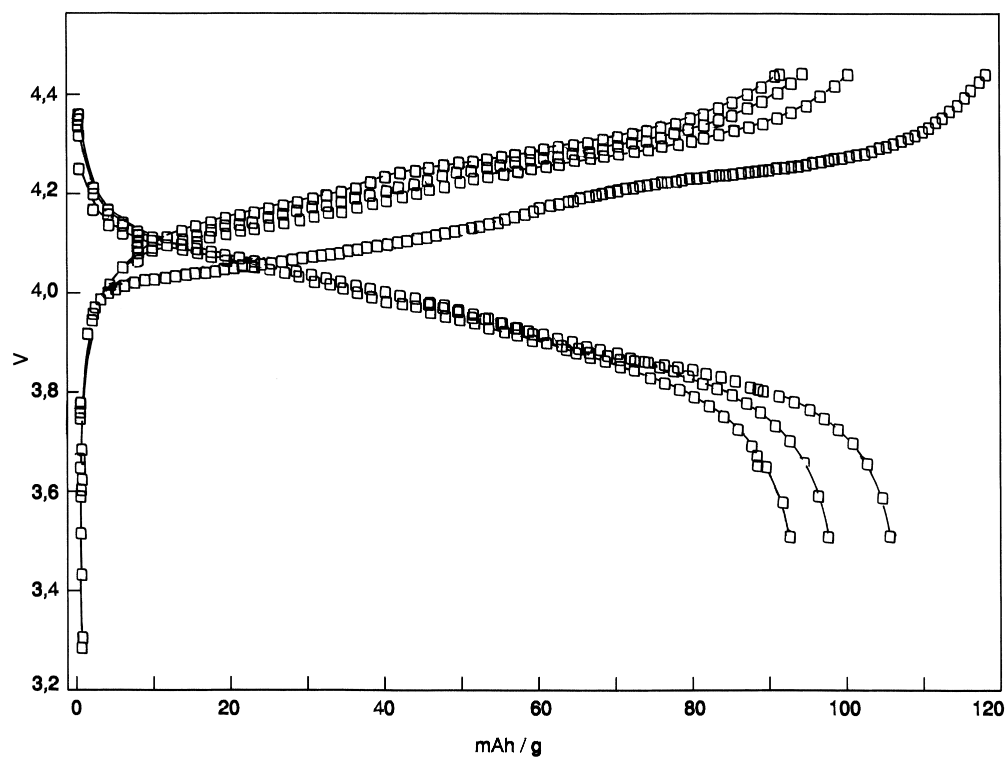

Fig. 7. Cycling behavior of $LiTi_{0.05}Mn_{1.95}O_4$.

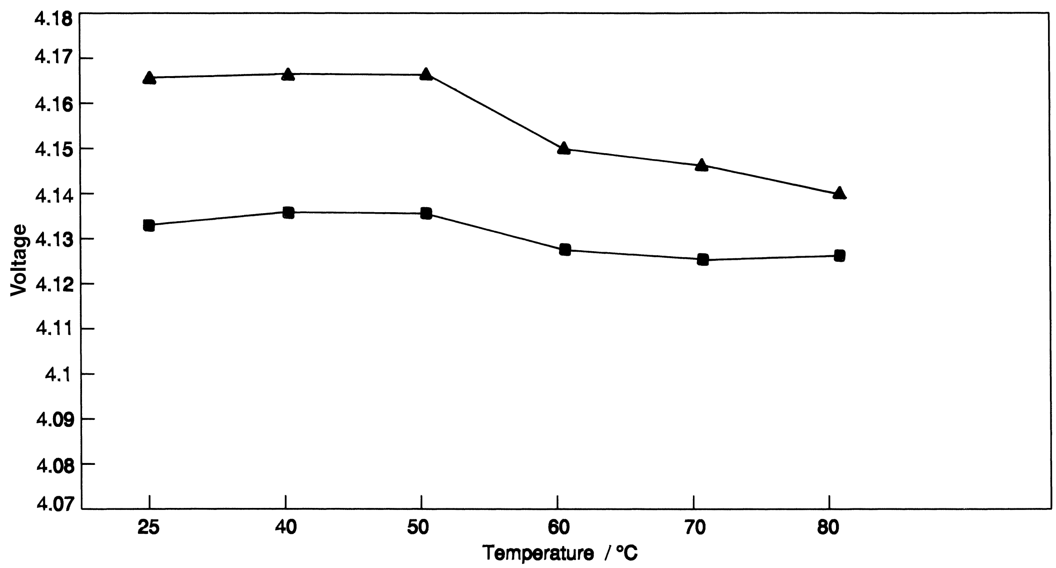

Fig. 8. Temperature dependence of open circuit voltage (OCV).

3. Results and discussions

The powder XRD pattern of the titanium doped $LiMn_2O_4$ spinel is presented in Fig. 1. The XRD patterns were similar to that of the $LiMn_2O_4$ standard and all samples were identified as single phase spinels. A slight variation in the lattice parameter *a* was observed (Table 1) which indicates a change during doping. Further, looking at the intensity of the 220 peak, it is observed that the dopant ions occupy only the 16*d* sites and not the 8*a* sites.

The cyclic voltammetric studies of the spinels indicate clear well defined anodic and cathodic peaks in the 4.1–4.15 V region indicating deintercalation and intercalation processes. Representative cyclic voltammograms of the spinels are presented in Figs. 2 and 3. Capacities of the spinels were calculated from the cyclic voltammograms and are presented in Tables 2 and 3.

Fig. 4 shows the charge and discharge curves of $Li/LiTi_{0.05}Mn_{1.95}O_4$ cells. The capacity of the spinels synthesized at low temperatures was obtained by cycling as well as from CV studies (Table 2). It must be considered that the electrochemical capacity of the spinel synthesized by the low temperature route is much lower than that of the reference material synthesized by the high temperature route (120 mAh g^{-1}). Further investigations have shown that the spinel (low temperature route) contained Mn_2O_3 as impurities. Similar reduced capacities for lower temperature spinels were observed by Song et al. [17]. Therefore, the above doped spinels were subjected to high temperature annealing. Furthermore, lithium manganese doped by a low and high content of titanium was also synthesized and scanned for its electrochemical behavior. It is interesting to note that $LiMn_2O_4$ doped with a low content of titanium ($Ti_{0.05}$) delivers the highest capacity similar to that of commercial lithium manganese powder. This observation is interesting in view of the fact that the ionic radii of Co^{3+}, Fe^{3+} are similar to that of Ti^{4+} (0.64 Å). The capacities obtained by CV and cycling studies (Table 3) are in agreement. Further, the XRD (Fig. 5) of the discharged product after 20 cycles still indicates spinel structure and hence, the material is capable of further cycling. In the light of the above, coin type cells were fabricated and their performance behavior evaluated by initially charging the cells at 0.5 mA up to 4.4 V. Further, these cells were subjected to charging and discharging at 1 mA current. These cells showed good cyclability. Table 4 projects the electrical characteristics of lithium ion cells as compared to cells fabricated using commercial lithium manganese oxide. The cycling behavior of $Li//LiMn_2O_4$ and $Li//LiTi_{0.05}Mn_{1.95}O_4$ coin type cell are presented in Figs. 6 and 7, respectively. Temperature dependence of the cell capacity was also carried out using commercial $LiMn_2O_4$ and $LiTi_{0.05}Mn_{1.95}O_4$. It is seen from Fig. 8 that the OCV of the cell remains stable from -30 to $+80^\circ C$ indicating the stability of the cell materials.

4. Conclusion

The above preliminary studies indicate that a low content of titanium doped in lithium manganese oxide spinels could be beneficial for use as a positive material for rechargeable lithium batteries.

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