Studies on chromium/aluminium-doped manganese spinel as cathode materials for lithium-ion batteries—A novel chelated sol–gel synthesis

R. Thirunakaran\textsuperscript{a,*}, A. Sivashanmugam\textsuperscript{a}, S. Gopukumar\textsuperscript{a}, Charles W. Dunnill\textsuperscript{b}, Duncan H. Gregory\textsuperscript{b}

\textsuperscript{a} Central Electrochemical Research Institute, Karaikudi 630 006, Tamil Nadu, India
\textsuperscript{b} University of Glasgow, Chemistry Department, Joseph Black Building, Glasgow G12 8QQ, United Kingdom

**Abstract**

Nanoparticles of LiMn\textsubscript{2}O\textsubscript{4}, LiCr\textsubscript{x}Mn\textsubscript{2−x}O\textsubscript{4} and LiAl\textsubscript{x}Mn\textsubscript{2−x}O\textsubscript{4} (x = 0.0–0.4) have been synthesized using either phthalic acid or fumaric acid as chelating agents, for the first time, through sol–gel method. These materials were characterized by thermo gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Electrochemical performance of these materials was assessed to use as cathode material for lithium-ion batteries. XRD patterns ascertain the formation of the phase pure compounds. SEM images indicate the nanosized nature of the particles with uniform morphology and texture. Doping of Cr/Al with the spinel resulted to increased agglomeration. Cr-doped spinel delivers 138 mAh/g while Al-doped spinel exhibit 139 mAh/g at the first cycle reversible capacity. Doping of 0.1 Al spinel cells shows superior performance over the tested 10 cycles in terms of low capacity fading. Co-doped Li\textsubscript{2.6}Co\textsubscript{0.4}N (x = 0.40) has also been synthesized by solid-state method to use as anode material for lithium-ion batteries. Cells were assembled with the synthesized spinel cathodes and these cells delivered stable specific capacity with high cumbic efficiency. Cyclic voltammograms of both spinels exhibit good oxidation and reduction peaks for Mn\textsuperscript{3+}/Mn\textsuperscript{4+}, Cr\textsuperscript{3+}/Cr\textsuperscript{4+} and Al\textsuperscript{3+}/Al\textsuperscript{4+}.

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1. Introduction

Pristine spinel LiMn\textsubscript{2}O\textsubscript{4} is one of the most promising candidates for rechargeable lithium batteries due its low cost, non-toxic nature and ease of preparation when compared with other layered oxides such as LiCoO\textsubscript{2} and LiNiO\textsubscript{2} (Tarascon et al., 1994; Gummow et al., 1994; Thackery et al., 1992). The capacity of spinel LiMn\textsubscript{2}O\textsubscript{4} upon repeated cycling decreases at elevated temperature which has been reported by several papers (Xia et al., 1997; Pistoia et al., 1996). The capacity fade is caused due to several factors such as Jahn-Teller distortion, two-phase unstable reaction (Gummow et al., 1994), slow dissolution of manganese into the electrolyte (Jang et al., 1996), lattice instability (Mehrotra and Jain, 1996), and particle size distribution (Ohuzuku et al., 1999). Of late, attempts were made to suppress the Jahn-Teller distortion for obtaining the high-cycling capacity during the repeated cycling. Several metal cations such as Co, Zn, Cu, Fe, Ni, Cr, Ti, and Al have been doped for Mn in LiMn\textsubscript{2}O\textsubscript{4} (Ohuzuku et al., 1999; Song et al., 1999; Lee et al., 2000). Further, it is shown that the
capacity fade of LiMn$_2$O$_4$ is often observed much in the 3V region which can be completely suppressed by doping selenium with LiMn$_2$O$_4$ (Park et al., 2000). In recent years, several low temperature preparation methods, viz., sol–gel method (Bach et al., 1990; Pereira-Romas, 1995), precipitation (Barboux et al., 1991) pechini process (Liu et al., 1996) and hydrothermal method (Whittingam, 1996) have been used to ascertain the physical and electrochemical properties of cathode material for rechargeable lithium-ion batteries.

Graphite (theoretical capacity 372 mAh/g) has been utilized as anode material in commercial Li-ion battery. Owing to demands of high-capacity secondary anode, lithium nitrides as new anode material with high capacity of 1024 mAh/g (Kang et al., 2003; Nishijima et al., 1991) have been used to ascertain the electrochemical properties of cathode material for rechargeable lithium-ion batteries.

In this work, an attempt has been made for the first time to inves-
tigate the electrochemical property of Li$_{2.6}$Co$_{0.4}$N/LiMn$_2$O$_4$, another attempt has been made for the first time to inves-
tigate the electrochemical property of Li$_{2.6}$Co$_{0.4}$N/LiCr$_{0.10}$Mn$_{1.90}$O$_4$ and Li$_{2.6}$Co$_{0.4}$N/LiAl$_{0.10}$Mn$_{1.90}$O$_4$ couples.

2. Experimental

Fig. 1 shows the flow chart for synthesis of LiM$_{x}$Mn$_{2-x}$O$_4$ (M = Cr/Al) $x = 0.1–0.4$ by a sol–gel method using phthalic acid/fumaric acid as a chelating agent. Stoichiometric amounts of lithium acetate, manganese acetate, chromium acetate/aluminium acetate and phthalic acid/fumaric acid were mixed thoroughly and dissolved in de-ionized water. This solution was stirred continuously with gentle heating till a homogeneous solution was obtained. Fifty millilitres of 1 M phthalic acid/fumaric acid was added to the solution and a thick pasty mass was obtained. During stirring pH was main-
tained between 5 and 6. Small amount of the paste was taken for TGA to study the associated thermal events during the sub-
sequent calcination process. The pasty precursor was dried overnight in an oven at 110°C for removing moisture and to get dried mass. The dried mass was ground and calcined at different temperatures, viz., 250, 450, 650 and 800°C for 4 h. The calcined samples were subjected to different physical (XRD, SEM, TEM, FT-IR) and electrochemical (CV, galvanostatic cycling) characterization.

2.1. Cell assembly

Coin cells of 2016 configuration were assembled using lithium metal as anode, Celgard 2400 as separator, 1 M solution of LiPF$_6$ in 50:50 (v/v) mixture of ethylene carbonate (EC) and diethyl-
ylene carbonate (DEC) as the electrolyte. The cathode was made through a slurry coating procedure from a mix containing active material powder, conducting black and poly(vinylidene fluoride) binder in N-methyl-2-pyrrolidone in the proportion 80:10:10, respectively. The slurry was coated over aluminium foil and dried at 110°C for 2 h. Slurry-coated aluminium foils were pressed at 10 tonnes kg/cm$^2$ for 2 min and 18 mm diameter electrodes were punched out and used as cathode. Coin cells were assembled in an argon filled glove box (MBraun, Germany) with moisture and oxygen levels maintained at less than 1 ppm. The cells were cycled at C/10 discharge rates in an in-house made battery testing unit. Cells employing nitride anodes were assembled in nitrogen filled glove box.

3. Results and discussion

3.1. Thermal studies

Fig. 2 shows TGA plot of spinel LiMn$_2$O$_4$ precursor. The TG curve depicts multiple weight loss regions. The meagre weight loss of 1% up to 200°C can be attributed to the removal of moisture. The following major weight loss regions observed between 200 and 700°C corresponding to a weight loss of 55% is associated with the decomposition of the acetate precur-
sors and chelating agent. Characteristic peaks corresponding to LiMn$_2$O$_4$ spinel starts appearing after 450°C. This can be supplemented from the XRD results (Fig. 4a). Gravimetrically stable region above 750°C declares the completion of the reac-
tion as can be ratified by the fingerprint peaks obtained for LiMn$_2$O$_4$ spinel calcined at 850°C.

Fig. 3a–d depicts thermo gravimetric analysis of Li$_{1-x}$Cr$_x$Mn$_{2-x}$O$_4$ precursors with Cr-doping levels ranging from 0.1 to 0.4. The TGA pattern of the Cr-doped spinel follows identical characteristic to that of parent LiMn$_2$O$_4$. The first weight loss region (4%) extending up to 300°C is accounted for the removal of moisture. Subsequent weight loss regions (58%) are observed beyond 400°C corresponding

Fig. 1 – Flow chart for the synthesis of cathode materials, viz., spinel LiMn$_2$O$_4$ and Li$_{1-x}$Cr$_x$Mn$_{2-x}$O$_4$: $x = $ Cr: 0.00–0.40; $y = $ Al: 0.00–0.40 by sol–gel method using either phthalic acid/fumaric acid as a chelating agent.
Fig. 2 – Thermo gravimetric analysis of spinel LiMn$_2$O$_4$ precursor.

to the decomposition of acetate precursors. Increase in chromium doping shows a marginal raise in weight loss. Thermal events cease beyond 800 °C.

TGA profiles of fumaric acid assisted LiAl$_x$Mn$_{2-x}$O$_4$ precursors with different Al-doping levels, viz., Al-0.10; Al-0.20; Al-0.30; and Al-0.40 are represented in Fig. 3e–h, respectively. TGA profiles follow a similar behaviour to that of parent LiMn$_2$O$_4$ and Cr-doped spinel. The initial removal of moisture (~4%) is extending up to 300 °C and ensuing weight loss zones (~50%) observed beyond 400 °C are assigned to the decomposition of acetate precursors extend up to 800 °C and thereafter the reaction concludes.

3.2. X-ray diffraction

XRD patterns of the sol–gel synthesized LiMn$_2$O$_4$ samples calcined at different temperatures, viz., as synthesized, 250, 450, 650 and 850 °C are shown in Fig. 4a. It is evident from the broad
and indistinct X-ray reflections obtained for as synthesized and low calcined (250 °C) sample shows amorphous nature of the compounds. However, XRD patterns of LiMn$_2$O$_4$ calcined at 450 °C and above depict the signature peaks corresponding to that of spinel with few odd reflections assignable to α-Mn$_2$O$_3$ and LiMn$_2$O$_4$ impurities. The spectral profiles of high heated levels, viz., 0.10, 0.20, 0.30 and 0.40 synthesized by sol–gel method and calcined at 850 °C. (c) XRD patterns of the fumaric acid assisted parent spinel LiMn$_2$O$_4$ and LiAl$_x$Mn$_{2-x}$O$_4$ different Al-doping levels, viz., 0.10, 0.20, 0.30 and 0.40 synthesized by sol–gel method and calcined at 850 °C.

Fig. 4a–d shows the XRD patterns of the phthalic acid assisted parent spinel LiMn$_2$O$_4$ and LiAl$_x$Mn$_{2-x}$O$_4$ different Al-doping levels, viz., 0.10, 0.20, 0.30 and 0.40 calcined at 850 °C. All the peaks for LiMn$_2$O$_4$ and LiAl$_x$Mn$_{2-x}$O$_4$ different Cr-doping levels, viz., 0.10, 0.20, 0.30 and 0.40 calcined at 850 °C. The peak signatures of the parent and chromium-doped compound match perfectly to Joint Committee on Powder Diffraction Standards (JCPDS) card no: 35-782. All the peaks are striking similarity with that of LiCr$_x$Mn$_{2-x}$O$_4$ (Lee et al., 2001; Fey et al., 2003). Further, higher intensity of (1 1 1) plane than the rest is an indicator of processing good electrochemical activity for lithium-ion batteries. It is quite interesting that phthalic acid chelating agent with LiCr$_x$Mn$_{2-x}$O$_4$ spinel forms chain formation, metal ligands easily between Mn–O and COO$^-$ group particles resulting in the formation of product which has been substantiated by the pointed reflections in the XRD pattern.

Fig. 4e shows the XRD patterns of the fumaric acid assisted parent spinel LiMn$_2$O$_4$ and LiAl$_x$Mn$_{2-x}$O$_4$ different Al-doping levels, viz., 0.10, 0.20, 0.30 and 0.40 calcined at 850 °C. All the peaks for LiMn$_2$O$_4$ and LiAl$_x$Mn$_{2-x}$O$_4$ confirming single phase of the spinel compound with out any impurities. Al-doped spinel shows without any impurity peaks compared with that of parent spinel which is in good agreement to other previous researchers (Hon et al., 2002). Highly crystalline compounds calcined at 850 °C were taken for further electrochemical studies such as charge–discharge and cyclic voltammograms.

3.3. SEM and TEM studies

Fig. 5a–d shows the SEM images of spinel LiMn$_2$O$_4$ particles calcined at different temperatures, viz., 250, 450, 650 and 850 °C, respectively. The LiMn$_2$O$_4$ grains calcined at 250 and 450 °C present as nanosized particles (~50nm) with uniform morphology. However, the snaps of high calcined samples at 650 and 850 °C (Fig. 5c and d) show irregular morphology and the particles are found to enlarge as sintered lumps upon increase in calcination temperature.

Fig. 5e–h illustrate the SEM images LiCr$_x$Mn$_{2-x}$O$_4$ particles with different Cr-doping levels (0.1, 0.2, 0.3 and 0.4) calcined at 850 °C. It is apparent that the particles of Cr-doped samples are with more uniform morphology than that of un-doped at all temperatures. The powders with Cr: 0.1 and 0.2 show particles below 50 nm size while the high chromium samples (Fig. 6c and d) show relatively bigger grains due to sintering of particles.

Fig. 6a–d shows the SEM images of Al-doped LiMn$_2$O$_4$ at different Al-stoichiometry (0.1, 0.2, 0.3 and 0.4) calcined at 850 °C. It is evident that the particles are of spherical grains with average size of ~50 nm at all dopant level of aluminium (x = 0.1–0.4). The particles are comparatively smaller than un-doped and Cr-doped counterparts. However, a low degree of enlargement in particle size is seen at high Al concentration.

Fig. 7 shows the TEM images of doped and un-doped LiMn$_2$O$_4$ particles. In the case of un-doped LiMn$_2$O$_4$, the average particle size of the compound calcined at 250 and 450 °C is found to be around 100 nm. Further, the particles depict individual grain morphology with well-separated grain boundaries and the grain size is found to be grown with increase in calcination temperature (650 and 850 °C). TEM images of particles with high chromium (0.40) present as well separated lines with individual grain morphology. In the case of Al-doped spinel also with increase in Al-doping (0.40) good agglomerated particles were observed. It is perceptible that doping certainly improves morphological refinement in obtaining compound without any impurities. The peak signatures of the parent and chromium-doped compound match perfectly to Joint Committee on Powder Diffraction Standards (JCPDS) card no: 35-782. All the peaks are striking similarity with that of LiCr$_x$Mn$_{2-x}$O$_4$ (Lee et al., 2001; Fey et al., 2003). Further, higher intensity of (1 1 1) plane than the rest is an indicator of processing good electrochemical activity for lithium-ion batteries. It is quite interesting that phthalic acid chelating agent with LiCr$_x$Mn$_{2-x}$O$_4$ spinel forms chain formation, metal ligands easily between Mn–O and COO$^-$ group particles resulting in the formation of product which has been substantiated by the pointed reflections in the XRD pattern.

Fig. 4b shows the XRD patterns of the phthalic acid assisted parent spinel LiMn$_2$O$_4$ and LiCr$_x$Mn$_{2-x}$O$_4$ different Cr-doping levels, viz., 0.10, 0.20, 0.30 and 0.40 synthesized by sol–gel method and calcined at 850 °C. All the peaks for LiMn$_2$O$_4$ and LiCr$_x$Mn$_{2-x}$O$_4$ confirm the formation of single-phase spinel
more individually defined texture in long-range order especially in the case of Al-doping.

3.4. FT-IR spectroscopy

Fig. 8 shows the FT-IR Spectra of un-doped and doped LiMn$_2$O$_4$ powders. In all the FT-IR reflections the broad IR band located at $\sim$3488 cm$^{-1}$ is attributed to the O–H stretching vibration in chelating acids. Bands corresponding to carboxylate anion (COO$^-$) were observed at 1670 and 1340 cm$^{-1}$. Further, it is evident from this IR spectral bands that with increasing temperature, the lower wavelength has been observed due to Li–O–Mn stretching vibration. Peaks around 5967–3469.312 cm$^{-1}$ invariably for all compounds indicating the presence of Li–O–H bond. The IR spectrum of undoped spinel shows peaks around 1670–1662 cm$^{-1}$ which are slightly shifted to higher to lower wave number due to Li–O. In the case of chromium-doped samples: Cr-0.10, 850; Cr-0.20, 850; Cr-0.30, 850; Cr-0.40, 850°C. Two bands obtained for the samples calcined at high temperature, shifted to higher frequencies. It is very clear that with increasing chromium contents higher wavelength has been observed due to Li–O–Mn (Cr-0.10 = 3475.9011; Cr-0.20 = 3475.0211; Cr-0.30 = 3476.7441 and Cr-0.40 = 3477.9911 cm$^{-1}$). Furthermore, peaks around 2947–2953 cm$^{-1}$ invariably for all compounds indicating the presence of Li–Cr–Mn–O. Also, IR spectrum of Cr-doped spinel shows peaks around 1661–1662 cm$^{-1}$ which are slightly shifted to lower to higher wave number due to Li–O–Cr. Spectroscopic studies on chromium-doped spinel LiMn$_2$O$_4$ for lithium-ion batteries has been investigated by Huang et al. (Wu et al., 2001). However, at the higher temperature, disappearances of peaks for lower wavelength which may be due to decomposition of acetate salt and chromium salt. Thus, all the vibrations of the bonds have been clearly investigated from FT-IR studies.

Also, in the case of aluminium-doped samples: Al-0.10, 850; Al-0.20, 850; Al-0.30, 850; Al-0.40, 850°C. The samples calcined at high temperature, the two bands in the spectra shifted to higher frequencies. It is very clear that with increasing aluminium contents higher wavelength has been observed due to Li–O–Mn (Al-0.10 = 3447.1347; Al-0.20 = 3455.8128; Al-0.30 = 3472.2046 and Al-0.04 = 3477.9911 cm$^{-1}$). Furthermore, peaks around 2947–2953 cm$^{-1}$ invariably for all compounds indicating the presence of Li–Al–Mn–O. Also, IR spectrum of Al-doped spinel shows peaks around 1652–1654 cm$^{-1}$ which is slightly shifted to lower to higher wave number due to Li–O–Al. However, at the higher temperature, disappearance of peaks for lowers wavelength which may be due to decomposition of acetate salt and chromium salt. Thus, all the vibrations of the bonds have been clearly investigated from FT-IR studies. The related FT-IR study on aluminium-doped LiNiO$_2$ has been investigated by Kalyani et al. (Kalyani et al., 2003).
3.5. Charge–discharge studies

First cycle charge–discharge curves and cycling performance of parent LiMn$_2$O$_4$ and LiCr$_x$Mn$_{2-x}$O$_4$ ($x=0.1–0.4$) are represented in Fig. 9a and b, respectively. During the first cycle un-doped spinel LiMn$_2$O$_4$ calcined at 850°C delivered discharge capacity of 135 mAh/g against the charging capacity of 145 mAh/g which corresponds to a Columbic efficiency of 93%. The discharge capacity stabilizes around 125 mAh/g in the 7th cycle and thereafter a fairly higher fading is observed over the
investigated 10 cycles the spinel electrode shows 34% capacity fade. In the case of Cr-doped spinel, it can be seen that LiCr$_{0.1}$Mn$_{1.90}$O$_4$ exhibits a stable cycling behaviour. The first charge capacity is around 145 mAh/g and the discharge capacity is 139 mAh/g yielding a columbic efficiency of 96%. It can be seen that the effect on Cr-doping to higher concentration (Cr = 0.4) is negative. Over the tested 10 cycles LiCr$_{0.1}$Mn$_{1.90}$O$_4$ cells experienced only 12% capacity fade. Further, these results are superior to those of earlier reports. Fey et al. and Popov et al. (Fey et al., 2003; Zhang et al., 1998) reported that chromium-doped spinel (Cr = 0.1) delivered discharge capacity around 120 and 125 mAh/g at the first cycles. Hence it is obvious that, phthalic acid assisted preparation produces electrochemically active species delivering stable cycling performance. 

Fig. 7 – TEM images of spinel LiMn$_2$O$_4$ particles calcined at different temperatures, viz., 250, 450, 650 and 850 °C. TEM images of LiCr$_x$Mn$_{2-x}$O$_4$ particles calcined at 850 °C with different Cr doping levels, viz., Cr-0.10; Cr-0.20; Cr-0.30 and Cr-0.40. TEM images of LiAl$_x$Mn$_{2-x}$O$_4$ particles calcined at 850 °C with different Al doping levels, viz., Al-0.10; Al-0.20; Al-0.30 and Al-0.40.

Fig. 10a and b depicts typical charge–discharge profiles and cycling characteristics of LiAl$_x$Mn$_{2-x}$O$_4$ (Al = 0.1–0.4) samples. Among the four concentrations of Al-doping, LiAl$_{0.10}$Mn$_{1.90}$O$_4$ cells show a columbic efficiency of 98% in the first cycle resulting from the ratio of discharge to charge capacity of 139 and 142 mAh/g. The cells show 9% capacity loss over 10 cycles. The cycling performance deteriorates in higher Al-doping level (Al = 0.4). These results are superior to those who had investigated earlier. Bao et al. reported in his work that LiAl$_{0.10}$Mn$_{1.90}$O$_4$ had delivered discharge capacity of ~122 mAh/g (Bao et al., 2006). Lee et al. (Lee et al., 2001) reported a discharge capacity of 121 mAh/g at the 10th cycle. Hence, synthesizing spinel using fumaric acid as chelating agent via sol–gel method originates high performing material.
Fig. 8 – FT-IR spectra of the sol-gel derived LiMn$_2$O$_4$ powders calcined at different temperatures (250, 450, 650 and 850 °C), Cr-0.10, 850; Cr-0.20, 850; Cr-0.30, 850 and Cr-0.40, 850 °C; Al-0.10, 850; Al-0.20, 850; Al-0.30, 850 and Al-0.40, 850 °C.

Fig. 9 – Charge-discharge behaviour of LiMn$_2$O$_4$ and LiCr$_x$Mn$_{2-x}$O$_4$ at different chromium dopant levels, viz., 0.10, 0.20, 0.30 and 0.40 and cycling behaviour of (a) LiMn$_2$O$_4$ and (b) LiCr$_x$Mn$_{2-x}$O$_4$ at different chromium dopant levels, viz., 0.10, 0.20, 0.30 and 0.40.
Several researchers have reported studies on lithium transition metal nitrides to use as an anode for lithium batteries. Suzuki et al. (Suzuki and Shodai, 1999) reported Li/Li$_{7-x}$MnN$_4$ electrode delivering maximum discharge capacity of 400 mAh/g. Gregory et al. investigated Li/Li$_{3-x-y}$N (x = Co: 0.4; y = Cu: 0.4) which delivered discharge capacity of 98 mAh/g at the first cycle against the charging capacity of 495 mAh/g (Gregory, 1999; Marterm’yanov et al., 1995). Much attention has been focused to ascertain entire structural families of nitride chemistry and electric and magnetic properties of Li$_{3-x}$Ni$_x$N and Li$_{3-x}$Co$_x$N. In this paper, charge–discharge characteristics of Li$_{2.6}$Co$_{0.4}$N/LiMn$_2$O$_4$; Li$_{2.6}$Co$_{0.4}$N/LiCr$_{0.1}$Mn$_{1.9}$O$_4$; Li$_{2.6}$Co$_{0.4}$N/LiAl$_{0.4}$Mn$_{1.6}$O$_4$; Li$_{2.6}$Co$_{0.4}$N/LiAl$_{0.1}$Mn$_{1.9}$O$_4$ couple exhibit discharge capacity of 1.9 mAh/g corresponding to columbic efficiency of 63%. Further, Li$_{2.6}$Co$_{0.4}$N/LiCr$_{0.1}$Mn$_{1.9}$O$_4$ couple exhibit discharge capacity of 3.25 mAh/g for 3.5 mAh/g charging given raise to columbic efficiency of 92.8%. In case of LiCr$_{0.1}$Mn$_{1.9}$O$_4$ (Fig. 11b) better discharge capacity has been obtained than parent compound. Further, higher doping of chromium (x=0.4) led to a fall in electrochemical performance (charging capacity: 2.8 mAh/g; discharge capacity: 1.75 mAh/g). From this it is clear that, the discharge capacity and columbic efficiency are decreased with the increase of dopant concentration.

The performance of nitrides with Al-doped spinel counterpart indicates that Li$_{A0.4}$Mn$_{1.6}$O$_4$ bestows discharge capacity of 3 mAh/g against charging capacity of 4.5 mAh/g corresponding to 66.6% columbic efficiency. Cells employing Li$_{A0.4}$Mn$_{1.6}$O$_4$ exhibit (Fig. 11d) discharge capacity of 5.8 mAh/g against 15 mAh/g charging capacity (columbic efficiency: 38.6%) while the same for

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**Fig. 10** – Charge–discharge behaviour of LiMn$_2$O$_4$ and LiAl$_{x}$Mn$_{2-x}$O$_4$ at different chromium dopant levels, viz., 0.10, 0.20, 0.30 and 0.40 and cycling behaviour of (a) LiMn$_2$O$_4$ and (c) LiAl$_{x}$Mn$_{2-x}$O$_4$ at different chromium dopant levels, viz., 0.10, 0.20, 0.30 and 0.40.
Al–0.4 stoichiometry is low. Although the capacities derived from the cells of nitride-spinel couples are disappointingly low—may be associated with optimization of nitride electrode constituents, preparation methods, etc., it is dispensable that the results are truly reflecting the trend and the studies are also first of its kind. Hence, from the above preliminary attempts, it can be suggested that Li$_{2.6}$Co$_{0.4}$N/LiCr$_{0.10}$Mn$_{1.90}$O$_4$ couple out performs Al-doped ones. This same trend has also been observed with the synthesized spinels when they are coupled with lithium as anode.

3.6. Cyclic voltammetry

Cyclic voltammogram of Li/LiMn$_2$O$_4$ obtained in the potential range 2.5–5.0 V at a scan rate of 1 mV s$^{-1}$ using Li as reference and counter electrode is presented in Fig. 12a. A single anodic peak observed at 4.75 V is corresponding to Mn$^{3+}$/Mn$^{4+}$ couple and a cathodic peak observed at 3.75 V is associated to Mn$^{4+}$/Mn$^{3+}$ couple. As the scan rate of 1 mV s$^{-1}$ is fairly high, two separate peaks for Mn$^{4+}$/Mn$^{3+}$ and Cr$^{3+}$/Cr$^{4+}$ appeared as a single broad peak. LiCr$_{0.1}$Mn$_{1.90}$O$_4$ spinel exhibits slightly higher cathodic peak current (1.75 mA) when compared to the un-doped one (1.45 mA). This observation suggests that low level of chromium doping in the spinel enhances better electrochemical performance (Sigala et al., 1995; Shu et al., 2003) of this compound. Fig. 12c depicts the cyclic voltammograms of Li/LiAl$_{0.10}$Mn$_{1.90}$O$_4$. Two well-defined anodic peaks are observed at around 3.2 and 4.5 V corresponding to Mn$^{3+}$/Mn$^{4+}$ and Cr$^{3+}$/Cr$^{4+}$ couple. A scan rate of 1 mV s$^{-1}$ is fairly high, two separate peaks for Mn$^{3+}$/Mn$^{4+}$ and Al$^{3+}$/Al$^{4+}$ couples. Several researchers reported that the reversibility of LiMn$_2$O$_4$ could be improved by various metal cations such as Co$^{2+}$, Ni$^{2+}$, Mg$^{2+}$, Cr$^{3+}$. This study suggests that low doping of aluminium ($x=0.1$) is found to be beneficial to derive better cycling characteristics as could be seen from the high cathodic peak current (1.5 mA) obtained for the above Al-concentration of the spinel.
4. Conclusions

An attempt has been made to produce manganese spinel cathode materials for lithium-ion battery through a sol–gel process chelated by either phthalic acid or fumaric acid for the first time. Cr and Al have been doped in four concentrations ($x = 0.1–0.4$). XRD, SEM and TEM studies confirm the formation of single-phase compound with fine individual morphology. Doping resulting to a lesser degree agglomerated orientation. The particles are found to be $\sim 50$ nm. FT-IR studies of LiCr$_x$Mn$_{2-x}$O$_4$ ($x = 0.0–0.4$) spinel structured compounds with single phase and nanosized particles for lithium rechargeable batteries. FT-IR studies of LiAl$_x$Mn$_{2-x}$O$_4$ ($x = 0.0–0.4$) spinel confirm the stretching and bending vibration of these compounds (Li–O–Al; Li–O–Mn; Li–Al–Mn–O; Li–Al–Mn–O). Un-doped spinel LiMn$_2$O$_4$ demonstrates 34% capacity fade over the investigated 10 cycles. In the case of Cr-doped spinel, it can be seen that LiCr$_{0.10}$Mn$_{1.90}$O$_4$ exhibits a stable cycling behavior. The first charge capacity is around 145 mAh/g and the discharge capacity is 139 mAh/g yielding a columbic efficiency of 96%. Among the four concentrations of Al-doping, LiAl$_{0.10}$Mn$_{1.90}$O$_4$ cells show a columbic efficiency of 98% in the first cycle resulting from the ratio of discharge to charge capacity of 139 and 142 mAh/g. The cells show 9% capacity loss over 10 cycles. Hence, synthesizing spinel using new chelating agents originates high performing material. Primarily, the doped and un-doped spinel compounds were coupled with Li$_{2.6}$Co$_{0.40}$N anodes and the charge–discharge characteristics indicates that Li$_{2.6}$Co$_{0.40}$N/LiCr$_{0.10}$Mn$_{1.90}$O$_4$ couple out performs Al-doped ones. Cyclic voltammograms of both spinels exhibit good oxidation and reduction peaks for Mn$^{3+}$/Mn$^{4+}$, Cr$^{3+}$/Cr$^{4+}$, and Al$^+$/Al$^{3+}$. LiAl$_{0.10}$Mn$_{1.90}$O$_4$ spinel exhibits slightly higher cathodic peak current around (1.5 mA) when compared to the un-doped one (1.45 mA).

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