Composite of Li-Rich Mn, Ni and Fe Oxides as Positive Electrode Materials for Li-Ion Battery

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A porous layered composite of Li3MnO2 and LiMn0.5Ni0.5Fe0.5O2 (composition: Li0.29Mn0.47Ni0.18Fe0.2O2) is prepared by reverse microemulsion method employing tri-block co-polymer, P068 as a soft-polymer template. The Co-free composite is studied as a cathode material for Li-ion battery. Several samples are prepared by heating the precursor in the temperature range between 500 and 900 °C. The N2 adsorption/desorption studies reveal that the product samples possess mesoporosity with broadly distributed pores around 15–50 nm diameter. Pore volume and surface area decrease by increasing the temperature of preparation. Charge-discharge, cycling and rate capability are investigated. The discharge capacity of the sample prepared at 900 °C is about 170 mAh g−1 at a specific current of 25 mA g−1 with a good cycling stability. A value of 140 mAh g−1 is obtained at the end of 50 charge-discharge cycles. Discharge capacity of 91 mAh g−1 is obtained at a specific current of 206 mA g−1. A high rate capacity of the composite is attributed to its porous nature.

Research activities on lithium-ion batteries have increased in the recent past because of their attractive energy density. In an extended range of applications, they are successful in small sizes at present and anticipated to be used in large sizes for applications such as electric vehicles. Although the energy density of the present Li-ion batteries is the greatest among rechargeable batteries, future requirements such as electric vehicle applications require still greater energy density. The next generation Li-ion batteries, thus, need novel electrode materials which can provide greater discharge capacity than the present materials. Compounds with a high atomic ratio of extractable lithium to transition metal are expected to provide high discharge capacity values. Li3MnO2 belongs to this category of materials. Li3MnO2 is a layered oxide similar to LiCoO2 and its formula can also be presented in the crystal lattice are occupied by Li atoms. On the basis of extraction Li(Li0.33Mn0.67)O2. One third of the octahedral sites meant for Mn in the crystal lattice are occupied by Li atoms. On the basis of extraction of the total available Li in Li3MnO2, a discharge capacity of 456 mAh g−1 is expected, provided the compound is electrochemically active. However, Li3MnO2 is not electrochemically active because of the oxidation state of Mn is +4 and it cannot increase to +5 when Li is extracted from the structure. Nevertheless, several publications have appeared with different procedures for activation of Li3MnO2 and with varying capacity values. The initial discharge capacity values are generally high for the activated phases of Li3MnO2, but cycling instability is observed in all reports. In order to enhance the cycling stability, composites of Li3MnO2 with other layered lithiated transition metal oxides such as LiCoO2 are studied. Intended to substitute Co in LiCoO2 by Mn and Li together (1 Co by 0.67 Mn + 0.33 Li) in a wide range of compositions. When cycled between 3.00 and 4.30 V, there was a decrease in discharge capacity with an increase in concentration of Mn and Li substituted for Co. Pure phase of LiCoO2 provided the highest capacity among several with an increase in concentration of Mn and Li substituted for Co. Between 3.00 and 4.30 V, there was a decrease in discharge capacity.

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inexpensive. Additionally, Fe is cheap because it is an earth abundant metal. By replacing Co with Fe in the above composition, the composite Li\textsubscript{1.2}Mn\textsubscript{0.53}Ni\textsubscript{0.13}Fe\textsubscript{0.13}O\textsubscript{2} is worthy to investigate. In the present study, porous Li\textsubscript{2}Mn\textsubscript{0.53}Ni\textsubscript{0.13}Fe\textsubscript{0.13}O\textsubscript{2} (composition: Li\textsubscript{2}Mn\textsubscript{0.53}Ni\textsubscript{0.13}Fe\textsubscript{0.13}O\textsubscript{2}) samples are prepared by inverse microemulsion route assisted by a soft polymer template, namely, F068. The composite samples possess mesoporosity and provide high discharge capacity, a high rate capability and also high cycling stability.

**Experimental**

For preparation of the composite, reverse microemulsion route involving poly(EO)	extsubscript{78}-poly(PO)	extsubscript{30}-poly(EO)	extsubscript{78}, where EO and PO are ethylene oxide and propylene oxide units, respectively, F068 (Aldrich) as a soft template is used. The oil and aqueous phases were prepared separately. The oil phase was prepared by dissolving 1.0 g F068 in a mixture of 51.2 ml cyclohexane (Merck) and 6.2 ml n-butanol (SD Fine Chemicals). Then 0.225 g lithium dodecylsulfate, LDS (Aldrich) was added and stirred for 3 h to get a transparent liquid. 1.072 g lithium nitrate (Aldrich), 1.596 g manganese nitrate tetrahydrate (SD Fine Chemicals) and 0.445 g nickel nitrate hexahydrate (SD Fine Chemicals) were dissolved in 15 ml double distilled water. The aqueous phase was transferred to the oil phase and stirred for 12 h by a magnetic pellet at ambient temperature. The emulsion was slowly evaporated at 110°C. A yellow color gel was obtained. The gel was heated in air at several temperatures between 500 and 900°C for 12 h. A brownish black colored powder sample was obtained. The synthesis is schematically shown in Fig. 1.

The powder XRD patterns were recorded using Philips X-Pertpro diffractometer at 45 kV and 30 mA using Cu K\textsubscript{α} (λ = 1.5418 Å) radiation source. Nitrogen adsorption-desorption isotherms were measured at −196°C by using Micromeritics surface area analyzer model ASAP2020. Surface area of composite samples was calculated using Brunauer-Emmett-Teller (BET) method in the relative pressure (p/p\textsubscript{0}) range 0.05–0.25 from adsorption branches of the isotherms. The pore size distribution was estimated by Barrett-Joyner-Halenda (BJH) method from the desorption branches. The morphology was examined using a FEI Co. scanning electron microscope (SEM) model Sirion and transmission electron microscope (TEM) model JEOL-JEM 2100F. The chemical composition and oxidation states of Mn, Ni and Fe on the surface of the nanostucture were examined by Thermofisher Scientific X-ray photoelectron spectroscopy (XPS) using X-ray Al anode (monochromatic K\textsubscript{α}, X-rays at 1486.6 eV) as the source. The C1s region was used as the reference and was set at 284.6 eV. Thermogravimetric analysis (TGA) was recorded from ambient temperature to 900°C at a heating rate of 10°C min\textsuperscript{-1} under the flow of O\textsubscript{2} gas by using thermal analyzer NETZSCH model TG 209 F1. The chemical composition analysis of the composite sample was carried out by inductive coupled plasma atomic emission spectroscopy using Varion inductive coupled spectrometer model Vista-PRO.

For the fabrication of electrodes, the active material (80 wt%), acetylene black, AB (Alfa Aesar) (10 wt%) and poly(vinylidene fluoride), PVDF (Aldrich) (10 wt%) were mixed in a mortar and a few drops of 1-methyl-2-pyrrolidinone, NMP (Aldrich) were added to obtain a slurry. A stainless steel disk (16 mm diameter) was cleaned with a detergent and water, etched in 30% dilute HNO\textsubscript{3} (SD Fine Chemicals), rinsed with double-distilled water followed by acetone and air dried. The slurry was applied on a cleaned stainless steel disk and dried at 110°C under vacuum for 12 h. The mass of active material was in the range 3–5 mg cm\textsuperscript{-2}. Lithium metal foil (0.75 mm thickness, Aldrich) was used as the counter electrode and a Celgard porous polypropylene membrane (2400) was used as a separator. A commercial electrolyte of 1M LiPF\textsubscript{6} dissolved in ethylene carbonate, diethyl carbonate and dimethyl carbonate (2:1:2 v/v) (Chameleon) was used as the electrolyte. Coin cells CR2032 (Hohsen Corporation, Japan) were assembled in an argon environment glove box MBraun model UNILAB.

The cells were subjected to galvanostatic charge-discharge cycling in the voltage range from 2.00 to 4.80 V at several current densities and also different temperatures. Cyclic voltammetry, charge-discharge cycling, rate capability and electrochemical impedance studies were carried out using Biologic potentiostat/galvanostat model VMP3. The electrochemical impedance experiments were carried out by using Solartron electrochemical interface model SI 1287 in an air-conditioned room at 22 ± 1°C.

**Results and Discussion**

**Synthesis.—** Soft chemical synthesis by inverse microemulsion route is useful for the preparation of small particles. When a small volume of an aqueous phase consisting of the reactants is dispersed in a large volume of a non-aqueous phase, the reactants are confined to micrometer sized aqueous reaction zones and the size of the product particles is limited to the size of the aqueous droplets, which are stabilized by surfactant molecules. Sub-micrometer/nanometer size product particles are synthesized by this route. The F068 is a polymer template of tri-block polymer with general formula -(EO)\textsubscript{78}-(PO)\textsubscript{30}-(EO)\textsubscript{78}, where EO and PO are ethylene oxide and propylene oxide, respectively. The presence of F068 in the reaction medium is expected to facilitate porosity on the product particles. The presence of hydrophilic EO block and hydrophobic PO block is responsible for generating porosity on the product particles. By combining the salient

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**Figure 1.** Schematic diagram of the composite Li\textsubscript{1.2}Mn\textsubscript{0.53}Ni\textsubscript{0.13}Fe\textsubscript{0.13}O\textsubscript{2} sample.
Thermogravimetric analysis.—The gel obtained at 110 °C was subjected to thermogravimetry (Fig. 2). There is a continuous loss of mass between the ambient and about 130 °C due to the removal of solvents. About 55% of weight loss is observed at 130 °C. There is about 27% of weight decrease between 130 and 270 °C, which is likely due to decomposition of nitrates and the polymer template. The mass of the sample is fairly constant between 270 and 900 °C. Therefore, samples of the gel were heated at different temperatures between 500 and 900 °C for 12 h. The composite Li1.2Mn0.53Ni0.13Fe0.13O2 samples prepared at 500, 600, 700, 800 and 900 °C are hereafter referred to as S5, S6, S7, S8 and S9, respectively.

XRD studies.—The XRD patterns (Fig. 3) of the samples prepared at different temperatures suggest that all samples are crystalline. The peaks present between 20 and 23° correspond to the superlattice ordering of Li and transition metals layers, which correspond to the features of inverse microemulsion and polymeric templates, synthesis of porous, sub-micrometer sized cathode materials, namely, LiFePO4, LiNi1/3Mn1/3Co1/3O2, Li2MnO3 and Li2MnO3-LiMn1/3Ni1/3Co1/3O2 were synthesized in our laboratory. A similar procedure was followed for preparation of Li2MnO3:LiMn1/3Ni1/3Fe1/3O2 in the present work.

Microscopy.—SEM micrographs of Li2MnO3:LiMn1/3Ni1/3Fe1/3O2 composite samples are shown in Fig. 4. The S5 sample consists of flakes with edges projecting upwards (Fig. 4a). On further heating the precursor at higher temperatures, the flakes tend to agglomerate as large sized globules at 600, 700 and 800 °C (Figs. 4b, 4c and 4d) and submicron sized particles (200–500 nm) with clear inter-particle separation are observed in the samples prepared at 900 °C (Fig. 4e). The chemical formula of sample S9 calculated from the results of ICP and EDXA spectrum is Li1.14Mn0.55Ni0.12Fe0.13O2, which agrees well with the intended composition. The TEM images (Figs. 5a–5e) indicate the presence of non-spherical particles and the particle size increases with an increase in temperature of preparation due to agglomeration, as expected.

Surface area and porosity.—Nitrogen adsorption/desorption isotherms and BJH porosity curves are shown in Fig. 6. The dominance of Li2MnO3 phase. The pair of peaks expected around 65° for a layered compound of α–NaFeO2 structure is not well resolved (Fig. 3 curves (ii) and (iii)) for the samples prepared at 500 and 600 °C. Thus, the S5 and S6 samples are not well formed layered compounds, although reflections due to any impurities are not observed. Nevertheless, XRD patterns of samples S7, S8 and S9 indicate that these samples are well formed layered crystalline compounds (Fig. 3 curves (iv), (v) and (vi)). Li2MnO3 is described as Li[Li1/3Mn2/3]O2 structure of O3-type where the octahedral sites of inter-slab are occupied by lithium ion and octahedral sites of the slab by lithium and manganese ions in 1:2 ratio. The XRD patterns (Fig. 3 curves (iv), (v) and (vi)) agree well with the standard pattern of Li2MnO3 (JCPDS file No. 84-1634) (Fig. 3 curve (i)).
adsorption and desorption branches do not merge in the pressure region \( p/p_0 \) between 0.60 and 0.99 for all samples suggesting porous nature of the samples. The amount of N\(_2\) adsorbed on S5 sample (Fig. 6ai) at \( p/p_0 = 0.99 \) is about 52 cm\(^3\) g\(^{-1}\). The BET surface area obtained in \( p/p_0 \) ratio 0.1–0.2 range of the adsorption isotherm is 10.6 m\(^2\) g\(^{-1}\). The porous nature of all samples is clearly reflected in BJH curves (Fig. 6b). There is a broad distribution of pores around 30 nm diameters for S5 sample (Fig. 6bi). The BET surface area and cumulative pore volume obtained for all samples are listed in Table I. The BET area obtained for S6 sample is also 9.2 m\(^2\) g\(^{-1}\), but pore volume decreases marginally (Table I and Fig. 6b). On further increasing the temperature of preparation, surface area of the sample S7 decreases to 6.4 m\(^2\) g\(^{-1}\). The decreasing tendency of both surface area and pore volume continues by increasing the temperature of preparation. The BET area of sample S9 is 1.8 m\(^2\) g\(^{-1}\). The BJH curves indicate the existence of porosity in all samples, although the pore volume decreases by increasing the temperature of preparation (Table I and Fig. 6b). Increase in particle size and also density on increasing the temperature of preparation could be the causes for a decrease in pore volume of the composite samples. Nevertheless, porosity is present on all samples, which is attributed to the presence of the polymeric template in the reaction medium of preparation.

**XPS studies.**—The XPS survey spectrum and also Mn 2p, Ni 2p and Fe 2p core level spectra of S9 sample are shown in Fig. 7. The survey spectrum (Fig. 7a) indicates the presence of elements Li, C, O, Mn, Ni, and Fe in the samples. A minor amount of C present on the surface of sample particles is due to decomposition of the polymer template used for the synthesis. The core level spectrum of Mn (Fig. 7b) is characterized by peaks at 642.20 eV for Mn 2p\(_{3/2}\) and 653.70 eV for Mn 2p\(_{1/2}\). The deconvolution of these peaks provides binding energy values of 643.15 eV and 654.40 eV corresponding to Mn\(^{4+}\) as the major oxidation state and 641.05 eV and 652.00 eV corresponding to Mn\(^{3+}\) as the minor oxidation state. In the Ni spectrum, Ni 2p\(_{3/2}\) and Ni 2p\(_{1/2}\) peaks are present (Fig. 7c). Additionally a satellite peak at 861.00 eV appears, which is attributed to multiple splitting in the energy level of Ni containing oxides. The best fit for the Ni 2p\(_{3/2}\) peak results in two binding energy values. The major peak at 854.00 eV and minor peak at 856.10 eV correspond to Ni\(^{2+}\) and Ni\(^{3+}\) oxidation states, respectively. Similar to Ni 2p\(_{3/2}\) peak, Ni 2p\(_{1/2}\) peak also provide Ni\(^{2+}\) major and Ni\(^{3+}\) minor oxidation states with the corresponding binding energy values of 871.00 eV and 872.80 eV. The Fe spectrum

![Figure 5. TEM images of (a) S5, (b) S6, (c) S7, (d) S8 and (e) S9 samples of composite Li\(_{1.2}\)Mn\(_{0.53}\)Ni\(_{0.13}\)Fe\(_{0.13}\)O\(_2\).](image)

![Figure 6. (a) N\(_2\) adsorption/desorption isotherms and (b) pore size distribution (BJH) curves of Li\(_{1.2}\)Mn\(_{0.53}\)Ni\(_{0.13}\)Fe\(_{0.13}\)O\(_2\) samples of S5 (i), S6 (ii), S7 (iii), S8 (iv) and S9 (v). The curve (v) is expanded and shown as inset in (b). In (a), curves (ii), (iii), (iv) and (v) are, respectively, vertically shifted by 5, 10, 15 and 20 units of Y-axis scale relative to the position of curve (i).](image)

| S. No | Sample | BET surface area (m\(^2\) g\(^{-1}\)) | BET surface area (cm\(^3\) g\(^{-1}\)) | Pore diameter (nm) |
|-------|--------|--------------------------------------|--------------------------------------|-------------------|
| 1     | S5     | 10.6                                 | 0.078                                | 30                |
| 2     | S6     | 9.2                                  | 0.062                                | 38                |
| 3     | S7     | 6.4                                  | 0.035                                | 15                |
| 4     | S8     | 3.8                                  | 0.023                                | 10                |
| 5     | S9     | 1.8                                  | 0.009                                | 16                |
The fit results of the 2p_{1/2} peak result in Fe oxidation states (viz., Mn^{+2} and Fe^{+3}) as the major oxidation state and Fe^{+2} (709.60 eV) as the minor oxidation state. Similarly, the fit results of Fe2p_{3/2} peak also provide Fe^{+3} (724.60 eV) and Fe^{+2} (722.70 eV) as the major and minor oxidation states, respectively. These results are similar to the results reported for composite oxide of Mn, Ni and Fe.33,45–49 The presence of minor oxidation states (viz., Mn^{+3}, Ni^{+3} and Fe^{+2}) is explained as due to valance degeneracy through dynamic equilibria.33

Cyclic voltammetry.—Cyclic voltammograms of S7, S8 and S9 samples recorded in the potential range between 2.0 and 4.8 V with scan rate 0.1 mV s^{-1} for three repetitive cycles are presented in Fig. 8. For S7 sample (Fig. 8a), an oxidation current peak appears at 4.18 V in the first cycle when the cell is subjected to potential sweep from the open-circuit voltage (≈ 3.30 V). This current peak is followed by another large current peak at 4.70 V. In the reverse sweep from 4.80 to 2.00 V, a small cathode current peak appears at 3.80 V. Among the three transition elements present in the composite, the oxidation state of Mn, Ni and Fe are +4, +2 and +3, respectively.33 Accordingly, the oxidation current peak at 4.18 V (Fig. 8a) is attributed to the extraction of Li^{+} from Li[Mn_{0.53}Ni_{0.13}Fe_{0.13}]O_{2} phase of the composite resulting from the oxidation of Ni^{+3} to Ni^{+2}.45 The oxidation current peak appearing at 4.70 V (Fig. 8a) is attributed to the activation of Li_{2}MnO_{2} phase present in the composite. The electrochemical activation of Li_{2}MnO_{2} occurs due to the loss of O_{2} as Li_{2}O from the surface of the particles.34,49

In the first reverse sweep from 4.80 to 2.00 V, three cathodic current peaks are expected. In the first cyclic voltammograms of S7 sample (Fig. 8a), the cathodic current peak at 3.80 V corresponding to the reduction of Ni^{+4} appears clearly and no other reduction peaks are noticed indicating that Mn and Fe are electrochemically inactive. On repeatedly recording the voltammograms (Fig. 8a), the 4.70 V oxidation peak is absent from the second cycle onwards and the 4.18 V oxidation peak shifts in the negative direction to 4.05 V with low intensity. Furthermore, a new oxidation peak starts evolving at 3.18 V. In the reverse direction of the second cycle, the 3.80 V peak starts decreasing and a new reduction current peak at 3.00 V starts evolving. The voltammogram of third cycle of samples S7 (Fig. 8a) confirms that 3.18 V oxidation peak as well as 3.00 V reduction peak become more intense. The pair peaks at 3.00 / 3.18 V is attributed to the reversible Mn^{4+/3+} and Mn^{3+/2+} redox couple, which becomes dominant subsequent to the oxidative activation step at 4.70 V. The 3.00/3.18 V peaks agree well with the differential capacity peaks reported by Croy et al.50 Thus, the voltammetric features of S7 sample reveal the electrochemical activation of the lithium rich composite leading to an integrated redox process.33,51

The cyclic voltammograms of S8 sample recorded for three repeated cycles (Fig. 8b) reflect the features of S7 sample (Fig. 8a), but with a few minor changes observed. The 4.05 V oxidation peak appears clearer and the 3.19 V oxidation peak as well as 3.07 V reduction peak become more intense in the second and third cycles (Fig. 8b) when compared with S7 sample (Fig. 8a). Thus, the cyclic voltammetric current features of S8 sample are more resolved than those of S7 sample. On the other hand, the cyclic voltammograms of S9 sample are

Figure 7. XPS patterns of Li_{1.2}Mn_{0.53}Ni_{0.13}Fe_{0.13}O_{2} sample S9. Survey spectrum (a), and core level spectra of manganese (b), nickel (c) and iron (d).
superior to those of both S7 and S8 samples in terms of sharpness of peaks as well as their reproducibility. The 3.08 V reduction peak formed in the second and third cycles are reproducible and well-resolved, in addition to the retention of 3.80 V for S9 sample (Fig. 8c), unlike the S7 sample with decreasing intensity of 3.80 V peak in the third cycle (Fig. 8a). The 4.05 V oxidation current peaks present in the second and third cycle voltammograms are well-formed. Thus, in all cases, there are two pairs of redox peaks, namely, 3.08/3.19 V and 3.80/4.05 V current peaks, which originate from Mn$^{3+}/^{4+}$ and Ni$^{2+}/^{3+}$ redox reactions, respectively, after the activation cycle. Thus, the voltammograms of S7, S8 and S9 samples suggest that the S9 sample is more electrochemically active and more reversible than the S7 and S8 samples. As expected, the charge-discharge cycling behavior of S9 sample is superior to S7 and S8 samples, as discussed below.

Charge-discharge cycling—Galvanostatic charge-discharge curves of S5–S9 samples for the first two cycles are shown in Fig. 9. It is observed that all samples are electrochemically active when cycled between 4.80 and 2.00 V. During the first charging of sample S5, two plateaus are observed, but voltage plateaus do not clearly appear during the discharge process (Fig. 9a). The differential plot (Fig. 9a inset) suggests that the transition from the first charging plateau to the second plateau in the first cycle occurs at 4.44 V. It is known that the oxidation states of Fe, Ni and Mn are $+3$, $+2$ and $+4$, respectively. The expected charging capacity from the oxidation of Ni$^{2+}$ to Ni$^{3+}$ in Li$_{1.2}$Mn$_{0.53}$Ni$_{0.13}$Fe$_{0.13}$O$_2$ thus becomes 82 mAh g$^{-1}$ of the composite. The value of the first plateau charge obtained for S5 sample is close to 82 mAh g$^{-1}$. Thus, the first plateau of the first charging process is attributed to the oxidation of Ni$^{2+}$ to Ni$^{3+}$. The second charging voltage plateau arises from the activation of Li$_2$MnO$_3$ part of the composite. In the second cycle, the charging potential curve is below that of the first cycle for S5 sample (Fig. 9a). Also, there is a single plateau, unlike two plateaus observed in the first charging. This is due to electrochemical activation of Li$_2$MnO$_3$ part during the first charge process, and subsequently integrating with LiMn$_{0.13}$Ni$_{0.13}$Fe$_{0.13}$O$_2$ part. The integrated active material thus exhibits a single plateau in the second cycle (Fig. 9a). It is also observed that the charge and discharge capacity values in the first cycle of S5 sample are 268 and 148 mAh g$^{-1}$, respectively, resulting in a coulombic efficiency of 0.55. On the other hand, the coulombic efficiency in the second cycle is 0.83 with charge and discharge capacity values of 160 and 133 mAh g$^{-1}$, respectively. The low efficiency of the first cycle is due to irreversible electrochemical activation of Li$_2$MnO$_3$. A marginal decrease in discharge capacity, but improved efficiency in the second cycle in relation to the first cycle is due to the activation of the composite and formation of integrated material. The charge-discharge voltage profiles of S6-S9 samples also are similar to those of S5 sample, but with minor changes (Figs. 9b–9e). As the sample preparation temperature increases (i.e., from sample S5 to S9), the voltage plateaus of both charge and discharge processes become more and more distinctly observed (Figs. 9a–9e insets). The charge-discharge coulombic efficiency in the first cycle is poor for S6-S9 samples, similar to that of S5 sample. However, there is an increase in efficiency to 0.82, 0.87, 0.92 and 0.98 for S6, S7, S8 and S9 samples, respectively, in the second cycle, with the respective discharge capacity values of 151, 152, 157 and 170 mAh g$^{-1}$. The discharge capacity of a cathode material depends on several properties, which include surface area, porosity, particle size, crystalline nature, etc. Small crystalline particles with large specific surface area and high pore volume are expected to deliver a high capacity. In the present study, there is a decrease in pore volume and also in surface area (Fig. 6 and Table I) by increasing the preparation temperature. Thus, the trends of variation of these properties are expected to favor decreased capacity for samples from S5 to S9, in contrast to the increased capacities obtained (Fig. 9). It is, therefore, likely that the crystallinity of the composite samples influences more than the rest of the properties, as the discharge capacity is found to increase with increased crystallinity of the samples in the present study (Fig. 3).

The integrated sample of Li$_2$MnO$_3$:LiMn$_{0.13}$Ni$_{0.13}$Fe$_{0.13}$O$_2$ prepared at 900°C in the present study delivers discharge capacity of 170 mAh g$^{-1}$, which is similar to or better than the reported values. Specific capacity values of 175 mAh g$^{-1}$ at current density 30 mA g$^{-1}$.
Figure 9. Charge-discharge voltage profiles of Li$_2$MnO$_3$:LiMn$_{1/3}$Ni$_{1/3}$Fe$_{1/3}$O$_2$ samples (a) S5, (b) S6, (c) S7, (d) S8 and (e) S9 in coin cells in the first and second cycle as indicated. Specific current: 25 mA g$^{-1}$; Electrode area: 2.0 cm$^2$ and mass of active material: 3–5 mg. Differential curves of the first and second cycle are shown as insets.

for a sample prepared by combustion method,
175 mAh g$^{-1}$ for a sample prepared by co-precipitation
and 120 mAh g$^{-1}$ for a sample prepared by co-precipitation method
are reported. The synthesis procedure used in the present study provides crystalline product with high porosity even at 900°C. Porosity of the material is desirable to facilitate volume changes that occur during Li$^+$-ion intercalation and de-intercalation stages and also a high rate capability. The superior performance of S9 is probably due to better crystallinity than the other samples. Amalraj et al., synthesized xLi$_2$MnO$_3$:(1-x)LiMn$_{0.33}$Ni$_{0.33}$Co$_{0.33}$O$_2$ (x = 0.3, 0.5 and 0.7) using self-combustion reaction in solution containing metal nitrates and sucrose.
Cycling performance, rate capability and impedance evolution of the electrodes were investigated. Structural changes occurring due to cycling were evaluated by XRD, Raman spectroscopy and $^7$Li magic angle spinning NMR techniques. The XRD pattern of the composite after repeated cycling indicated that the reflections related to Li$_2$MnO$_3$ component disappeared and the intensity of the main (003) reflection decreased substantially. This was attributed to complete extraction of Li$^+$ during prolonged charging of the electrode at 4.8 V. These observations were supported by Raman spectroscopy. A decrease in Raman spectrum peak intensities of the charged electrode was correlated with an increase in electronic conductivity of the delithiated electrode. A low discharge capacity of Li$_2$MnO$_3$: LiMn$_{1/3}$Ni$_{1/3}$Fe$_{1/3}$O$_2$ (170 mAh g$^{-1}$) in comparison with Li$_2$MnO$_3$:LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ (220 mAh g$^{-1}$) unless CC License in place (see abstract).
The discharge capacity is almost constant. The capacity values obtained second cycle for S8 and S9 samples. From the second cycle onwards, charge-discharge cycles (Fig. 10a), whereas the cells of sample S9 were repeated for 50 cycles (Fig. 10b) at a specific current of 30 mA and 176 mAh g$^{-1}$ than the S5–S7 samples (Fig. 9a). The capacity decreases from 165 to 148 and 160 mAh g$^{-1}$ of the first cycle to about 157 and 170 mAh g$^{-1}$ in the second cycle for S8 and S9 samples. From the second cycle onwards, the discharge capacity is almost constant. The capacity values obtained for S8 and S9 samples in the 30th cycle, respectively, are 64 and 84% of the values obtained in the first cycle. A stable discharge capacity of 140 mAh g$^{-1}$ is obtained for the composite sample prepared at 900 °C. The data of two more cells of the sample S9 for 50 cycles (Fig. 10b) further confirm that the sample S9 has higher stability with an excellent reproducibility. Differential capacity plots of one of the cells from the charge/discharge data of 2nd and 50th cycles are shown in Fig. 9b inset. The 2nd cycle data indicates a major oxidation peak at 3.8 V and a minor oxidation peak at 3.25 V (Fig. 10b inset). However, the minor 3.25 V peak becomes more intense in the 50th cycle, probably, due to transformation of the layered compound into the spinel phase.

**Cycle-life test.**—Cycle-life test results of the composite samples are shown in Fig. 10. All samples were subjected to continuous 30 charge-discharge cycles (Fig. 10a), whereas the cells of sample S9 were repeated for 50 cycles (Fig. 10b) at a specific current of 30 mA g$^{-1}$. The capacity values of S5, S6, and S7 decrease gradually from the initial values of 175, 148 and 160 mAh g$^{-1}$ to 78, 78 and 80 mAh g$^{-1}$, respectively, at the end of 30 charge-discharge cycles. The capacities, thus, decrease from their initial values by 45, 52 and 50% at the end of 30 charge-discharge cycles for S5, S6 and S7 samples, respectively. Nevertheless, the capacity values of S8 and S9 samples are more stable than the S5–S7 samples (Fig. 9a). The capacity decreases from 165 and 176 mAh g$^{-1}$ of the first cycle to about 157 and 170 mAh g$^{-1}$ in the second cycle for S8 and S9 samples. From the second cycle onwards, the discharge capacity is almost constant. The capacity values obtained for S8 and S9 samples in the 30th cycle, respectively, are 64 and 84% of the values obtained in the first cycle. A stable discharge capacity of 140 mAh g$^{-1}$ is obtained for the composite sample prepared at 900 °C. The data of two more cells of the sample S9 for 50 cycles (Fig. 10b) further confirm that the sample S9 has higher stability with an excellent reproducibility. Differential capacity plots of one of the cells from the charge/discharge data of 2nd and 50th cycles are shown in Fig. 9b inset. The 2nd cycle data indicates a major oxidation peak at 3.8 V and a minor oxidation peak at 3.25 V (Fig. 10b inset). However, the minor 3.25 V peak becomes more intense in the 50th cycle, probably, due to transformation of the layered compound into the spinel phase.

**Rate capability.**—Rate capability of S7, S8 and S9 composite samples was studied by subjecting the cells to charge-discharge cycling at several specific currents at room temperature (Fig. 11a). There is a decrease in discharge capacity of the three samples with an increase in current density, as expected. At all current densities, the capacity of S9 sample is the highest in agreement with the cyclic voltammetry (Fig. 8) and cycle-life test results (Fig. 10). About 100 mAh g$^{-1}$ is obtained for S9 sample at a specific current of 206 mA g$^{-1}$. Coin cells assembled with S9 sample was subjected to rate capability test at different temperatures also. The results are shown in Fig. 11b. As expected, the discharge capacity increases with an increase in temperature at all current density values.

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**Figure 10.** (a) Cycle life test of Li$_2$Mn$_{1/2}$Ni$_{1/3}$Fe$_{1/3}$O$_2$ samples S5 (i), S6 (ii), S7 (iii), S8 (iv) and S9 (v) and (b) cycle-life test of the sample S9, on two other cells over 50 charge-discharge cycles to verify reproducibility of the data at specific current of 25 mA g$^{-1}$. Electrode area: 2.0 cm$^2$ and mass of active material: 3–5 mg. Differential curves of cell 1 for the 2nd and 50th cycle are shown as inset in (b).

**Figure 11.** Rate capabilities of (a) Li$_2$Mn$_{1/2}$LiMn$_{1/3}$Ni$_{1/3}$Fe$_{1/3}$O$_2$ sample S7 (i), S8 (ii) and S9 (iii); and (b) Li$_2$Mn$_{1/2}$LiMn$_{1/3}$Ni$_{1/3}$Fe$_{1/3}$O$_2$ sample S9 at different temperatures: 5°C (i), 22°C (ii), 35°C (iii) and 55°C (iv). Specific currents used for charge-discharge cycling of the coin cells are indicated in mA g$^{-1}$. Electrode area: 2.0 cm$^2$ and mass of active material: 3–5 mg.
is expanded and shown as inset (Fig. 12c). There is a good agreement between the experimental impedance spectrum and theoretical spectrum. The low frequency linear spike data are used to calculate diffusion coefficient of Li$^+$ in the compound from Equation 1.

$$D_{Li^+} = \frac{R^2T^2}{2A^2F^2\sigma^2}$$  \[1\]

where $R$ is the gas constant, $T$ is absolute temperature, $A$ is the area of the electrode, $F$ is Faraday’s constant, $c$ is concentration of Li-ion. The value of $\sigma$ is obtained from the slope of plot $Z'$ versus $\omega^{-1/2}$ ($\omega = 2\pi f$, $f$ being the ac frequency), as shown in Fig. 12d. The value of $D_{Li^+}$ obtained is $3.45 \times 10^{-12}$ cm$^2$ s$^{-1}$. Similar values are reported for Li excess Mn oxides.56-59

**Conclusions**

A layered composite of Li$_2$MnO$_3$ and LiMn$_{0.33}$Ni$_{0.33}$Fe$_{0.33}$O$_2$ (composition: Li$_{1.2}$Mn$_{0.53}$Ni$_{0.13}$Fe$_{0.13}$O$_2$) was prepared successfully by polymer template method. The product samples prepared at different temperatures possessed mesoporosity with broadly distributed pores around 10–45 nm pore diameter. The BET surface area and pore volume decreased by increasing the temperature of preparation. Nevertheless, the electrochemical activity of the composite was greater for high temperature samples. The discharge capacity of the samples prepared at 900 °C was about 170 mAh g$^{-1}$ at 25 mA g$^{-1}$ with an excellent cycling stability. A discharge capacity of 92 mAh g$^{-1}$ was obtained at a specific current of 206 mA g$^{-1}$. The high rate capability was attributed to porous nature of the composite samples.

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**Figure 12.** (a) Nyquist impedance spectrum, (b) electrical equivalent circuit and (c) expanded high frequency semicircle region of S9 sample. Electrode area: 2.0 cm$^2$ and mass of active material: 3–5 mg. Experimental data are shown by open circle (○) and fit data are show by solid lines. The values of $R_{Q1}$, $R_f$ and $R_{Q2}$ are 4.8, 10 and 45 $\Omega$, respectively. (d) plot of real part $(Z')$ versus $\omega^{-1/2}$ in low frequency region.

**Ac impedance studies.—**A cell with S9 sample was assembled and subjected to a charge-discharge cycle at a specific current of 25 mA g$^{-1}$. The cell was allowed to reach an equilibrium voltage (3.45 V) and ac impedance was measured over a frequency range 100 kHz-10 mHz. Electrochemical impedance spectrum in Nyquist form is shown in Fig. 12a. Although, it is the impedance of the cell, the major contribution is considered from the cathode material. This is because fast kinetics of Li electrode reaction. The high frequency intercept provides the ohmic resistance of the cell. The diameter of the semicircle is a measure of solid electrolyte interface (SEI) layer resistance and charge-transfer resistance. The low frequency linear spike is due to diffusion limited Warburg resistance. The basic features of impedance spectrum are comparable with the data reported in the literature for cathode materials.27,28 The impedance spectrum (Fig. 12a) was subjected to non-linear least square fit procedure55 employing the electrical equivalent circuit shown in Fig. 12b. $R_{Q1}$, $R_f$, and $R_{Q2}$ refer to ohmic resistance, SEI layer resistance and charge-transfer resistance, respectively. $Q_1$ and $Q_2$ are constant phase elements corresponding to the capacitance of SEI layer and double-layer capacitance, respectively.56 W is Warburg impedance. The values of impedance parameters are listed in the caption of Fig. 12. The spectrum generated from the fit results is shown as solid curve, which passes through the experimental data points shown as open circles. The high frequency semicircle
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