Stable nickel-substituted spinel cathode material (LiMn$_{1.9}$Ni$_{0.1}$O$_4$) for lithium-ion batteries obtained by using a low temperature aqueous reduction technique

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A nickel substituted spinel cathode material (LiMn$_{1.9}$Ni$_{0.1}$O$_4$) with enhanced electrochemical performance was successfully synthesized by using a locally-sourced, low-cost manganese precursor, electrolytic manganese dioxide (EMD), and NiSO$_4\cdot$6H$_2$O as a nickel source by means of a low temperature aqueous reduction synthesis technique. This synthesis protocol is convenient to scale up the production of the spinel cathode material, with minimal nickel content (Ni = 0.1) in the structure, for lithium-ion battery applications. Ni-ions substituting Mn-ions was confirmed using XRD, EDS, XPS and electrochemical performance studies. LiMn$_{1.9}$Ni$_{0.1}$O$_4$ materials showed an octahedral shape with clearly exposed (111) facets that enhanced the Li-ion kinetics and improved the cycling performance compared to the pristine spinel sample (LiMn$_2$O$_4$). The LiMn$_{1.9}$Ni$_{0.1}$O$_4$ sample exhibited superior capacity retention by retaining 84% of its initial capacity (128 mA h g$^{-1}$) whereas pristine LiMn$_2$O$_4$ retained only 52% of its initial capacity (137 mA h g$^{-1}$). XPS confirmed that the Mn$^{3+}$/Mn$^{4+}$ ratio changed with nickel substitution and favored the suppression of capacity fading. The study clearly suggests that the integration of small amounts of Ni into the spinel structure is able to eliminate the disadvantageous Jahn–Teller effects in the LiMn$_2$O$_4$.

Introduction

Lithium-ion battery (LIB) technology is well-developed for portable electronic devices (like cellphones, laptops, iPads, etc.) which have been widely used. However, to implement LIBs for large-scale high-power systems such as plug-in hybrid electric vehicles (PHEVs) or plug-in electric vehicles (PEVs), there is a great need to increase the energy and power capabilities of these batteries. A nickel substituted LiMn$_2$O$_4$ (i.e., LiMn$_{2-x}$Ni$_x$O$_4$) has emerged as one of the promising spinel cathode materials for lithium-ion batteries. A member of the family is the high-voltage spinel LiMn$_{1.3}$Ni$_{0.7}$O$_4$ (LMNO) is considered as one of the most promising cathode materials for Li-ion batteries. In comparison with the commercial LiCoO$_2$ positive electrode, LiMn$_{1.3}$Ni$_{0.7}$O$_4$ has been shown to intercalate–deintercalate Li$^+$ ions at very high potential ($E = 4.7$ V vs. Li$^+$/Li). It has a large high intrinsic rate capability offered by the 3-dimensional lithium-ion diffusion in the spinel lattice. Besides, it is much safer, low-cost, and greener. There is a continued need to reduce the cost of the LiMn$_{1.3}$Ni$_{0.7}$O$_4$ by the use of low-cost synthesis method, the use of low-cost manganese precursor (such as the electrolytic manganese oxide, EMD) as well as drastic reduction in the amount of the expensive nickel in the structure (Ni < 0.5), without compromising its advantageous properties.

In this work, the preparation and electrochemical properties of LiMn$_{1.9}$Ni$_{0.1}$O$_4$ cathode materials containing very small amount of nickel ($x = 0.1$) and using EMD precursor have been investigated. The spinel cathode material was chosen due to its low toxicity, abundant material source and its high specific capacity of 148 mA h g$^{-1}$. The commercial spinel cathode material (LiMn$_2$O$_4$) is a well-studied cathode system for LIB with the potential to serve as an alternative to the toxic and expensive LiCoO$_2$. However, the main challenge with LiMn$_2$O$_4$ is the capacity fading due to Jahn–Teller distortion in the 3 V region, which is due to the generation of new phases during cycling and disproportionation reaction. In order to overcome this limitation, we have adapted a Ni-doping strategy. Literature reports have shown that doping with a small amount of Cr$^{3+}$, Ni$^{2+}$ and Al$^{3+}$ can stabilize the spinel structure of LiMn$_2$O$_4$ and provides high operating voltage above 4.7 V, suppress the Jahn–Teller effect, and improve the cycling properties. Although the use of small amount of nickel in the structure ($i.e.$, Ni < 0.5) has rarely been studied, it has been established that Ni = 0.1 provides the best electrochemistry. Therefore, there is a need to further explore the performance of this spinel using new low-cost synthetic routes.
Various synthetic routes have been followed to synthesize different spinel cathode materials, including solid state,\textsuperscript{17} combustion,\textsuperscript{18} co-precipitation,\textsuperscript{19} sol–gel method\textsuperscript{20} and modified pechini.\textsuperscript{21} Unfortunately these methods require elevated temperatures as high as 700–900 °C. Further, LiMn\textsubscript{2−x}Ni\textsubscript{x}O\textsubscript{4} synthesized by the solid-state method is often accompanied by the formation of Li\textsubscript{2}NiO\textsubscript{2} impurity phases which causes capacity fading. The crystallinity of the materials is also poor and leads to the dissolution of crystal faces by an electrolyte which deteriorates the rate capability. The techniques based on the processes of co-precipitation can give single phase LiMn\textsubscript{2−x}Ni\textsubscript{x}O\textsubscript{4} at lower temperatures. However, these methods involve the use of expensive reagents with complex process.\textsuperscript{22}

In this work, for the first time, we opted for a low temperature aqueous reduction method\textsuperscript{23} to synthesize LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} cathode materials. We have used NiSO\textsubscript{4}·6(H\textsubscript{2}O) as the nickel source and locally-produced low-cost EMD as the Mn source. This synthesis method not only has the advantage of using a locally-produced low-cost EMD but can also be a viable replacement to co-precipitation technique.

### Experimental

#### Materials and preparation

Electrolytic manganese dioxide (EMD) from a South African supplier (Delta EMD Pty Ltd) and LiOH·H\textsubscript{2}O, NiSO\textsubscript{4}·6(H\textsubscript{2}O), glucose from Sigma Aldrich were used for the synthesis of spinel LiMn\textsubscript{2−x}Ni\textsubscript{x}O\textsubscript{4} (x = 0 and 0.1) cathode materials.

Both LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} and its pristine material, LiMn\textsubscript{2}O\textsubscript{4} (for comparison) were prepared using a facile and low temperature aqueous reduction synthesis method by employing electrolytic manganese dioxide (EMD), LiOH·H\textsubscript{2}O, NiSO\textsubscript{4}·6(H\textsubscript{2}O) (for the Ni-doped sample) and glucose as a reducing agent. Briefly, a stoichiometric amount of LiOH·H\textsubscript{2}O, EMD and NiSO\textsubscript{4}·6(H\textsubscript{2}O) (for the LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} sample) was dissolved in 60 mL of double-distilled water by continuous stirring at a temperature of 80 °C. After 1 h, the appropriate amount of glucose dissolved in 20 mL of double-distilled water was added to the mixture. The stirring was continued for a further 8 h at 80 °C until the reaction was complete. The slurry was allowed to cool and settle for 12 h. After decanting, the product was washed several times with distilled water and dried at 120 °C. The resultant powder was calcined at 780 °C for 20 h in air and then cooled to room temperature naturally in the furnace. The purpose of further calcination at 780 °C to 20 h is to generate the required phase structure and composition in the LiMn\textsubscript{2−x}Ni\textsubscript{x}O\textsubscript{4} product (x = 0 and 0.1). In both samples, the same method of synthesis was adopted.

#### Equipment and procedure

The morphology of the samples LiMn\textsubscript{2−x}Ni\textsubscript{x}O\textsubscript{4} (x = 0 and 0.1) were obtained using a high resolution scanning electron microscope (JEOL, JSM-7600F), operating at an accelerating voltage of 5 kV. The EDS facility attached to the SEM gave the elemental data on the samples. The structural properties of the samples were investigated by X-ray diffraction analysis using a PANalytical X’Pert PRO PW3040/60 X-ray diffractometer with a Ni filtered Cu-Kz (\(\lambda = 0.154 \text{ nm}\)) monochromated radiation source. Data were collected in the 2θ range of 10–90° at a scan rate of 2° min \(^{-1}\). The XPS data were analyzed using the XPS Peak 4.1 program.

#### Cell fabrication and electrochemical analysis

Electrochemical cells were fabricated as follows: coin cells of 2032 were assembled using lithium metal as anode, Celgard 2400 as separator and a 1 M solution of LiPF\textsubscript{6} in ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) (1:1:1, by volume) the electrolyte. The cathode was made from a slurry using a 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 overnight for 12 h. The 18 mm diameter slurry-coated aluminium foil 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 charge-discharge cycles of the cells were carried out between 3.5–4.8 V at 0.2C rate with respect to their corresponding theoretical capacities of LiMn\textsubscript{2}O\textsubscript{4} and LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} using a Maccor 4000 series 96-channel battery tester. The electrochemical impedance spectroscopy studies were carried out using a Bio-Logic VMP 3 Potentiostat/Galvanostat controlled by EC-Lab v10.40 software. EIS data were collected after ageing the fabricated lithium-ion cell for 24 h. Nyquist plots of the charged and discharged electrodes were recorded after allowing 1 h of stabilization.

### Results and discussion

#### Morphological and EDS elemental analysis

Fig. 1a and b shows SEM images of LiMn\textsubscript{2}O\textsubscript{4} and LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} samples, respectively. The SEM image in Fig. 1b shows that the LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} cathode materials have octahedral shape with clearly exposed (111) facets. The (111) facets are known to allow the formation of a thinner solid electrolyte interphase (SEI) than other facets thereby enhancing the Li-ion kinetics and cycling performance.\textsuperscript{24}

The estimated particle size distribution\textsuperscript{25} of the compositions LiMn\textsubscript{2}O\textsubscript{4} and LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} is graphically presented in Fig. 1. Fig. 1c and d indicates that the particle sizes of the cathode materials are in the range of 0.30–0.50 μm for LiMn\textsubscript{2}O\textsubscript{4} and 0.80–1.80 μm for LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4}. The calculated average particle sizes of the samples LiMn\textsubscript{2}O\textsubscript{4} and LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} are 0.405 and 1.332 μm, respectively.

Energy-dispersive X-ray spectroscopy (EDS) elemental analysis was carried out in order to confirm the doping of Ni-ions. Table 1 displays the EDS elemental percentage of the samples. The EDS confirms that pristine LiMn\textsubscript{2}O\textsubscript{4} and Ni-doped LiMn\textsubscript{1−y}Ni\textsubscript{y}O\textsubscript{4} spinel cathode materials were successfully synthesized using our aqueous reduction techniques. The EDS indicated that the nickel elemental quantity increases from 0.06
for pristine LiMn$_2$O$_4$ to 1.62 for nickel substituted LiNi$_{0.1}$Mn$_{1.9}$O$_4$. The presence of carbon is due to the graphite-coating used in the SEM analysis.

**Structural characterisation**

The X-ray diffraction patterns to analyse the crystallographic structure and the impurity phases of the doped compounds synthesized by the aqueous reduction process are shown in Fig. 2. It is confirmed from the XRD patterns that the spinel LiMn$_2$O$_4$ phase (JCPDS File no. 88-1749) which indexes to a cubic spinel structure with a space group $Fd\bar{3}m$ is formed for both pristine LiMn$_2$O$_4$ and nickel substituted LiMn$_{1.9}$Ni$_{0.1}$O$_4$ samples. The calculated lattice constants of LiMn$_2$O$_4$ and LiMn$_{1.9}$Ni$_{0.1}$O$_4$ are 8.239 and 8.234 Å respectively. The decrease in the lattice constant of the LiMn$_{1.9}$Ni$_{0.1}$O$_4$ is due to the replacement of the Mn$^{3+}$ of high ionic radius ($r$(Mn$^{3+}$) = 72.0 pm) with Ni of smaller ionic radius (62.0 pm). Also, the XRD data for the precursor EMD, LiMn$_2$O$_4$ and LiMn$_{1.9}$Ni$_{0.1}$O$_4$ before 780 °C heat treatment are shown in Fig. 2b. The XRD peaks shifted slightly towards left with respect to EMD precursor reflection peaks, indicating structural change due to aqueous reduction reaction.

Fig. 3a and b shows the detailed XPS spectra of the Mn 2p$_{3/2}$ peaks of the LiMn$_2$O$_4$, and LiMn$_{1.9}$Ni$_{0.1}$O$_4$ samples, respectively. There is a broad peak width for both the materials, which indicates that the Mn exist in more than one oxidation state. The deconvoluted peaks of Mn 2p$_{3/2}$ for the samples LiMn$_2$O$_4$ and LiMn$_{1.9}$Ni$_{0.1}$O$_4$ with the obtained binding energy positions

| Sample       | C K  | O K  | Mn K | Ni K | Total% |
|--------------|------|------|------|------|--------|
| LiMn$_2$O$_4$| 15.89| 31.98| 52.08| 0.06 | 100    |
| LiMn$_{1.9}$O$_4$| 8.68 | 40.80| 48.86| 1.62 | 100    |

Fig. 3 The X-ray photoelectron spectra of the (a) LiMn$_2$O$_4$ and (b) LiMn$_{1.9}$Ni$_{0.1}$O$_4$ showing the Mn 2p$_{3/2}$ peak.
and cation distribution are summarised in Table 2. The binding energy peak positions corresponding to Mn\(^{4+}\) and Mn\(^{3+}\) are in agreement with previously reported values in the literature.\(^{25}\) The XPS results indicate a decrease in the Mn\(^{3+}\) for the Ni-doped LiMn\(_{1.9}\)Ni\(_{0.1}\)O\(_4\) cathode material that confirms a possible substitution of the Mn\(^{3+}\) by the Ni ions\(^{26,27}\) and results in an increase in Mn valence from 3.51 of LiMn\(_2\)O\(_4\) to 3.53 of LiMn\(_{1.9}\)Ni\(_{0.1}\)O\(_4\). This slight increase in Mn valence is needed for stabilising the spinel structure and suppressed the John–Teller distortion associated to capacity fading.\(^{27}\)

### Table 2 XPS (Mn-2p\(^{3/2}\) spectra) data of the LiMn\(_2\)O\(_4\) and LiMn\(_{1.9}\)Ni\(_{0.1}\)O\(_4\) samples

| Sample                  | Binding energy position (eV) | Cation distribution | Mn valence |
|-------------------------|------------------------------|---------------------|------------|
| LiMn\(_2\)O\(_4\)       | 641.3                        | Mn\(^{4+}\): 639.99  | 51.06      |
| LiMn\(_{1.9}\)Ni\(_{0.1}\)O\(_4\) | 641.5                        | Mn\(^{3+}\): 640.0  | 52.16      |

Electrochemical performance

**Galvanostatic charge/discharge experiments.** The main objective of Ni substitution into a spinel LiMn\(_2\)O\(_4\) cathode using small amounts of Ni is to achieve an improved electrochemical performance. The successful doping with nickel which was confirmed from the EDS, XRD and XPS data as described above, is indeed reaffirmed by an improvement in the electrochemical performance.

The electrochemical activity role is played by Mn\(^{3+}\) in the pristine LiMn\(_2\)O\(_4\). In the synthesized spinel, the Mn oxidation state is 3.5+ since an equal number of Mn\(^{3+}\) and Mn\(^{4+}\) are assumed to be present before charging. During charging, all Mn\(^{3+}\) convert ideally to Mn\(^{4+}\) by driving all Li\(^+\) ions into the anode electrode. The dissolution of manganese into the electrolyte is generated by the occurrence of the disproportion reaction 2Mn\(^{3+}\) (solid) → Mn\(^{4+}\) (solid) + Mn\(^{2+}\) (solution) in the 4 V region. As a result the electrochemical active Mn\(^{3+}\) will diminish accordingly the discharge capacity will start to fade.

The galvanostatic charge/discharge capacity performance of the cathode materials was carried out at 0.2C rates with respect to their corresponding theoretical capacities. The representative 1st, 2nd, and 40th cycle charge/discharge capacities of LiMn\(_2\)–\(x\)Ni\(_x\)O\(_4\) (\(x = 0\) and 0.1) are displayed in Fig. 4. During the first cycle the as-synthesized cathode materials LiMn\(_2\)O\(_4\) and LiMn\(_{1.9}\)Ni\(_{0.1}\)O\(_4\) respectively delivered discharge capacities of 137 mA h g\(^{-1}\) and 128 mA h g\(^{-1}\). The result shows that the initial discharge capacity decreases for the nickel-doped sample as expected. This trend of decrease in capacity is as a result of a reduction in the reversibly extractable Li\(^+\) ions from 1 for pristine LiMn\(_2\)O\(_4\) to 1 – \(x\) for Ni-substituted lithium manganese oxides upon substitution of the electrochemically active Mn\(^{3+}\) ions.\(^{28}\) The discharge capacities of the as-synthesized cathode materials are comparable to experimentally reported values.\(^{29,30}\)

![Fig. 4](image-url) The 1st, 2nd, and 40th cycle charge–discharge capacities of synthesized spinel (a) LiMn\(_2\)O\(_4\) and (b) LiMn\(_{1.9}\)Ni\(_{0.1}\)O\(_4\) cathode materials obtained at 0.2C.

![Fig. 5](image-url) The discharge capacity vs. cycle number for LiMn\(_2\)O\(_4\) and LiMn\(_{1.9}\)Ni\(_{0.1}\)O\(_4\) at (a) 0.2C and (b) 0.4, 0.8, 1, 2, 3C.
Despite that nickel insertion into EMD is difficult, it is interesting to see that our synthesis protocol was able to insert some amount that could successfully suppress the capacity fading. The capacity contribution at high voltage 4.5–4.7 V due to Ni$^{2+}$/Ni$^{4+}$ is very little, most of the electrochemical capacity is at the 4.1 V due to the Mn$^{3+}$/Mn$^{4+}$ redox couple. In addition, the first cycle charge–discharge reversibility for the samples LiMn$_2$O$_4$ and LiMn$_{1.9}$Ni$_{0.1}$O$_4$ is 86.9% and 69.7%, respectively. By considering the 2$^{\text{nd}}$ and 40$^{\text{th}}$ cycle capacity, it is noted that LiMn$_{1.9}$Ni$_{0.1}$O$_4$ shows gain in charge–discharge reversibility of 87% and 96% at the 2$^{\text{nd}}$ and 40$^{\text{th}}$ cycle, respectively. The improvement in reversibility arises from structural stability; at the 1–2 cycles, the spinel cathode material is not properly equilibrated with the electrolyte, but this should expected to improve upon repetitive cycling, and hence the improved reversibility.

Cycling stability and rate capability. To compare the performance of the two spinel materials, we first examined their cycling performance at 100 cycles at constant rate (0.2C). As evident in Fig. 5a, the nickel-substituted sample, LiMn$_{1.9}$Ni$_{0.1}$O$_4$, exhibited high cycling performance compared to its pristine counterpart. The capacity retention of LiMn$_{1.9}$Ni$_{0.1}$O$_4$ is about 84% compared to the 52% capacity retention recorded for the pristine LiMn$_2$O$_4$ after the 100 repetitive cycling at room temperature.

Next, we look at the rate capability of the two spinel materials by performing experiments at different high rates, from 0.4 to 3C (Fig. 5b). Upon completion of the rate capability experiments and the initial rate of 0.4C was repeated, LiMn$_{1.9}$Ni$_{0.1}$O$_4$ lost about 7% of its initial capacity (ca. 90 vs. 84 mA h g$^{-1}$) while the LiMn$_2$O$_4$ experienced a loss of about 16% (ca. 74 vs. 62 mA h g$^{-1}$), clearly confirming the improved electrochemical stability due to the presence of the Ni in the LiMn$_{1.9}$Ni$_{0.1}$O$_4$. Also, in all cases, the capacity of the LiMn$_{1.9}$Ni$_{0.1}$O$_4$ is almost double to that of the LiMn$_2$O$_4$; for example at 1C, the capacities of the LiMn$_{1.9}$Ni$_{0.1}$O$_4$ and LiMn$_2$O$_4$ are approximately 78 and 40 mA h g$^{-1}$, respectively.

To further prove the stability of LiMn$_{1.9}$Ni$_{0.1}$O$_4$, we carried out SEM analysis after 100 cycles. From the SEM images of LiMn$_2$O$_4$ (Fig. 6a) and LiMn$_{1.9}$Ni$_{0.1}$O$_4$ (Fig. 6b) samples after 100 cycles, it is interesting to observe that the morphology of the LiMn$_{1.9}$Ni$_{0.1}$O$_4$ showed a microporous but inter-connected network structures compared to the morphology of the LiMn$_2$O$_4$ that showed huge agglomeration of the starting nanoparticles. The morphology of the LiMn$_{1.9}$Ni$_{0.1}$O$_4$ should allow for a more facile electrochemistry (in terms of stability and kinetics) than that of the agglomerated. From the above experimental findings, we can conclude that the high electrochemical performance of the LiMn$_{1.9}$Ni$_{0.1}$O$_4$ over its pristine counterpart LiMn$_2$O$_4$ can be related to a considerable decrease in the Jahn–Teller distortion spinel.$^{15,31}$

Fig. 6 The SEM images of the (a) LiMn$_2$O$_4$ and (b) LiMn$_{1.9}$Ni$_{0.1}$O$_4$ after 100 cycles at 0.2C.

Fig. 7 Electrochemical impedance spectrum for LiMn$_2$O$_4$ and LiMn$_{1.9}$Ni$_{0.1}$O$_4$ samples (a) before, (b) after 100 cycles, and inset the equivalent circuit used to interpret the impedance spectra.
**Electrochemical impedance spectroscopy.** Electrochemical impedance spectroscopy is a powerful technique to study the kinetics of lithium intercalation/de-intercalation processes. EIS was carried out to examine the electrode resistance changes for LiMn2O4 and nickel substituted LiMn1.9Ni0.1O4 samples synthesized using nickel sulphate as nickel source. The Nyquist plots of pristine LiMn2O4 and LiMn1.9Ni0.1O4 are presented in Fig. 7 and the equivalent circuit used is shown in Fig. 7b inset. The intercept at the real (Z) axis in high frequency corresponds to the series resistance due to anode-separator-electrolyte-cathode (R). The R and CPE are the surface film resistance and film capacitance. The semicircle in the middle frequency range indicates the charge transfer resistance (Rct) and CPE is the double layer capacitance at the electrolyte–electrode interface. The inclined straight line relates to the Warburg impedance (Zw) and represents the diffusion impedance. The parameters of the equivalent circuit obtained from computer simulations for the as-synthesized LiMn2O4 and LiMn1.9Ni0.1O4 is shown in Table 3. Using the fitting, the Rct value of the LiMn2O4 and LiMn1.9Ni0.1O4 samples were found to be 373 and 235 Ω (before 100 cycles), 1105 and 431 Ω (after 100 cycles), respectively. These results confirm that the nickel substitution suppressed the charge transfer resistance, which contributed to a higher discharge capacity and better capacity retention after 100 cycles compared to the pristine LiMn2O4 sample. Molecules with smaller particles are expected to give better electrochemical kinetics. It is therefore surprising to observe that LiMn1.9Ni0.1O4 with larger average particle size (1.332 μm) gave an enhanced kinetics compared to the LiMn2O4 (0.405 μm). The interpretation may be found from the SEM images of the two electrodes where the morphology of LiMn1.9Ni0.1O4 showed porous and inter-connected networks that allow for electrochemistry to occur more effectively than an agglomerated and bulky morphology.

Plots of −Z’ vs. ω−1/2 for LiMn2O4 and LiMn1.9Ni0.1O4 (x = 0, 0.1) is shown in Fig. 8. The diffusion coefficients for LiMn2O4 and LiMn1.9Ni0.1O4 cathode materials are 6.4 × 10−12 and 6.89 × 10−11 cm2 s−1 at room temperature, respectively. The result confirms that nickel substitution has significantly enhanced the Li+ ion diffusion, which is a magnitude higher for nickel substituted LiMn1.9Ni0.1O4 than the pristine LiMn2O4 diffusion coefficient.

**Conclusions**

In summary, we employed low-cost manganese precursor electrolytic manganese dioxide (EMD) and a low temperature aqueous reduction synthesis technique to successfully prepare nickel substituted spinel LiMn2−xNiO4 (x = 0 and 0.1) cathode for lithium-ion battery by using NiSO4·6H2O as nickel source. We have confirmed that the Ni-ions substituted the Mn-ions using XRD, EDS, XPS and electrochemical performance studies. The nickel-substituted sample LiMn1.9Ni0.1O4 exhibited superior capacity retention as compared to pristine LiMn2O4; LiMn1.9Ni0.1O4 retained 84% of its initial capacity whereas pristine LiMn2O4 retained only 52% of its initial capacity.

The study shows that the use of a small amount of Ni to eliminate the Jahn–Teller effects of the LiMn2O4. In addition, this synthesis protocol has a great potential to be deployed for upscale-up production of pristine and Ni-doped spinel LiMn2O4 cathode materials for lithium-ion battery applications from locally-sourced and low-cost manganese precursor.

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![Table 3](image-url)

**Table 3** Fitting results of Nyquist plots of as-synthesized LiNi0.5Mn2−xO4 (x = 0, 0.1) cathode materials

|            | R0 (Ω)   | Rf (Ω)   | CPEf (µF) | n          | CPEd (mF) | Rct (Ω) | Zw (Ω s−1/2) |
|------------|----------|----------|-----------|------------|-----------|---------|--------------|
| **Before 100 cycles** |          |          |           |            |           |         |              |
| LiMn2O4    | 37.04 ± 0.72 | 25.85 ± 2.32 | 15.17 ± 0.96 | 0.84 ± 0.13 | 28.37 ± 2.89 | 373.1 ± 2.68 | 42.62 ± 2.51 |
| LiMn1.9Ni0.1O4 | 33.82 ± 0.23 | 21.51 ± 0.95 | 73.54 ± 3.26 | 0.56 ± 0.21 | 58.42 ± 8.26 | 235.8 ± 1.78 | 86.79 ± 3.57 |
| **After 100 cycles** |          |          |           |            |           |         |              |
| LiMn2O4    | 28.05 ± 1.66 | 304 ± 2.57  | 32.95 ± 2.04 | 0.77 ± 0.18 | 16.61 ± 4.56 | 1105 ± 2.34 | 17.54 ± 0.78 |
| LiMn1.9Ni0.1O4 | 24.92 ± 3.19 | 277.91 ± 1.69 | 28.77 ± 3.6  | 0.68 ± 0.05 | 27.29 ± 9.76 | 431.8 ± 7.94 | 11.38 ± 0.57 |

Fig. 8 Plots of −Z’ vs. ω−1/2 for LiMn2O4 and LiMn1.9Ni0.1O4.
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