1. INTRODUCTION

Different types of active materials have been studied for both the positive and the negative electrodes in lithium rechargeable batteries [1-5]. Over the last few years, much work was devoted to the material/chemical aspects of LiMn$_2$O$_4$, LiNiO$_2$, and LiCoO$_2$ compounds [6]. Among all these systems, the LiMn$_2$O$_4$ system remains the most attractive in terms of cost, abundance, and non-toxicity. It has been found, however, that the capacity of LiMn$_2$O$_4$ is lower than those of the other systems. The theoretical capacity is about 143 mAh g$^{-1}$ [7-9]. Due to its electronic configuration, $t_{2g}^3e_{g}^1$, Mn$^{3+}$ can induce Jahn–Teller distortion [10]. It is well known that manganese ions in LiMn$_2$O$_4$ are in two oxidation states, consisting of 50% Mn$^{3+}$ and 50% Mn$^{4+}$. When the amount of Mn$^{3+}$ is more than 50%, the spinel LiMn$_2$O$_4$ is apt to exhibit Jahn–Teller distortion [11]. During the discharge process, especially at high rates, the diffusion rate of lithium ions in the electrolyte solution is much more rapid than inside the spinel LiMn$_2$O$_4$ particle [12]. In non-equilibrium dynamic conditions, lithium ions heap up at the surface of spinel LiMn$_2$O$_4$ particles. In addition, Mn$^{3+}$-rich regions are formed in this process, which induces Jahn–Teller distortion. To inhibit the Jahn–Teller distortion, many research groups have tried to dope the Mn sites with other cations (Co, Ni, Cr, Fe, Cu, Mg, Al, etc.) and improved the cell capacity, as well as the cycling performance, over that of pure spinel LiMn$_2$O$_4$ [11-16]. This approach can partially reduce the Jahn–Teller distortion of spinel LiMn$_2$O$_4$ because it reduces the Jahn–Teller active Mn$^{3+}$ content [17, 18].

There are many papers on metal cation-doped LiMn$_2$O$_4$, and these papers usually focus on improving the electrochemical performance and electronic conductivity of LiMn$_2$O$_4$ via doping with one or two cations, such as Ni, Co, Cr, Zn, etc. These efforts have achieved some success. Dahn et al. showed that lithium deintercalation from LiNi$_{0.5}$Mn$_{1.5}$O$_4$ occurs at a potential of 4.6 - 4.7 V vs. Li$^+$ [19]. This reaction is attributed to the oxidation of Ni$^{3+}$ to Ni$^{4+}$. LiNi$_{0.4}$Mn$_{1.6}$O$_4$ was prepared under air and oxygen atmospheres using fine Mn$_2$O$_4$ particle and large MnO$_2$ particle at various temperatures [20]. The sample prepared from Mn$_2$O$_4$ at 750 °C under...
air or oxygen atmosphere exhibited an ideal electrochemical behavior. Electrochemical reactions of \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) are well explained based on three redox couples of \( \text{Mn}^{3+}/\text{Mn}^{4+} \), \( \text{Ni}^{2+}/\text{Ni}^{3+} \), and \( \text{Ni}^{2+}/\text{Ni}^{4+} \) by considering a presence of oxygen defects.

It was also reported that \( \text{LiCu}_{0.75}\text{Mn}_{2.5}\text{O}_4 \) (0.1 \( \leq x \leq 0.5 \)) showed a reversible electrochemical reaction at 4.95 \( V \), which was attributed to the oxidation-reduction of \( \text{Cu}^{2+}/\text{Cu}^{3+} \) [21-23]. Research has been focused on the \( \text{LiCu}_{0.25}\text{Mn}_{1.5}\text{O}_4 \) system and its doped counterpart with Ni cations, \( \text{LiN}_{i_{0.37}}\text{Cu}_{0.37}\text{Mn}_{1.25}\text{O}_4 \) (0 \( \leq x \leq 0.5 \)) spinel [23, 24]. Electrochemical results showed that the inclusion of Ni in the Cu-modified spinel increases the overall reversible capacity from 72 \( \text{mAhg}^{-1} \) for \( \text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) to 120 \( \text{mAhg}^{-1} \) for the spinel \( \text{LiN}_{i_{0.37}}\text{Cu}_{0.37}\text{Mn}_{1.5}\text{O}_4 \).

However, to the best of our knowledge there has been no attempt to investigate the electrochemical performance and behavior of \( \text{LiCu}_{0.25}\text{Co}_{0.25}\text{Mn}_{1.25}\text{O}_4 \) as a multi-doped \( \text{LiMn}_2\text{O}_4 \) compound.

### 2. EXPERIMENTAL

#### 2.1. Material preparation and sample characterization

\( \text{LiMn}_2\text{O}_4 \), \( \text{LiNi}_{0.75}\text{Mn}_{1.25}\text{O}_4 \), \( \text{LiCo}_{0.75}\text{Mn}_{1.25}\text{O}_4 \), \( \text{LiCu}_{0.75}\text{Mn}_{1.25}\text{O}_4 \), \( \text{LiCo}_{0.37}\text{Ni}_{0.37}\text{Mn}_{1.25}\text{O}_4 \), \( \text{LiCu}_{0.37}\text{Ni}_{0.37}\text{Mn}_{1.25}\text{O}_4 \), \( \text{LiN}_{i_{0.25}}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4 \) and \( \text{LiCo}_{0.25}\text{Cu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.25}\text{O}_4 \) cathode material samples, labeled respectively as A, 1-6 and B were prepared by a sol-gel process [25]. Stoichiometric amounts for the above compounds of \( \text{Li}_2\text{CO}_3 \) (SD Fine Chem. Ltd.), \( \text{Mn} (\text{CH}_3\text{CO}_2)_{2} \), \( \text{Cu} (\text{CH}_3\text{CO}_2)_{2} \cdot 4\text{H}_2\text{O} \) (Polarabo), \( \text{Ni} (\text{CH}_3\text{CO}_2)_{2} \cdot 4\text{H}_2\text{O} \) (Aldrich), and \( \text{Co} (\text{CH}_3\text{CO}_2)_{2} \cdot 4\text{H}_2\text{O} \) (Aldrich) were dissolved in the proper amounts, in separate dilute solutions of acetic acid or distilled water. About 50 ml ethanol was introduced into a mixture, which was heat-treated at 80 \(^\circ\text{C}\) for 4 h. Ammonia solution (28 - 30\%) was added to adjust the solution pH to 5.5. After that, glycine was added at twice the molar fraction of the starting materials, and the mixture was heated until a gel was formed [1]. The mixture was further heated to dryness, cooled, and ground into powder. The powder was transferred into a furnace and heated for 12 h in air at 800 \(^\circ\text{C}\).

Determination of the chemical composition of the prepared compounds was carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer Optima 2000 DV). The samples were investigated by X-ray diffraction (XRD) using a Siemens diffractometer. Brunauer-Emmett-Teller (BET) surface area analysis was carried out using a Quantachrome Nova Instrument. Scanning electron microscopy (SEM) was carried out by using Joel SEM-Model 5040. Electron spin resonance (ESR) spectra were collected by using a Bruker ESR spectrometer at 293 K.

#### 2.2. Electrochemical measurements

Active material powders, carbon black, and polytetrafluoroethylene (PTFE) binder were mixed in a weight ratio of 85:5:10, respectively, to fabricate composite positive electrode material with homogeneous mixing in a mortar and pestle (agate type). The mixture was blended with a suitable amount of N-methyl-2-pyrrolidone (NMP) to yield homogeneous slurry. The slurry was then spread onto Al foil substrates. The area of a coated electrode was 1 cm\(^2\), and the weight of the active material was about 5 mg. The electrodes were dried at 120 \(^\circ\text{C}\) for 8 h in a vacuum oven. The electrodes were then pressed under a mechanical pressure of 1500 kg/cm\(^2\). Coin cells were assembled in argon filled glove box. The two electrodes were the active material electrode (working electrode) and lithium metal ribbon (Sigma-Aldrich) as both counter and reference electrode. The separator was a circular foil of microporous polypropylene. The electrolyte was 1 M \( \text{LiClO}_4 \) dissolved in a 1:1 mixture of propylene carbonate (PC) and dimethyl carbonate (DMC). All potentials were recorded vs. Li/Li\(^+\) electrode. Cyclic voltammetry (CV) measurements were performed using a Multistat CHI 660 Electrochemical Workstation at a 0.1 mVs\(^{-1}\) scanning rate, with a potential window of 2.5 to 5.5 V vs.

<table>
<thead>
<tr>
<th>Sample (S)</th>
<th>Unit cell lattice [Å]</th>
<th>Cell volume [Å(^3)]</th>
<th>FWHM β [°]</th>
<th>Selected 2θ [°]</th>
<th>Crystallite size (L) [nm]</th>
<th>Surface area [m(^2)g(^{-1})]</th>
<th>Strain (ε) \times 10(^3)</th>
<th>Dislocation density δ [m(^{-2})] \times 10(^{16})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<td>555</td>
<td>0.413</td>
<td>44.066</td>
<td>20.09</td>
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<td>1.8017</td>
<td>1.6365</td>
</tr>
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<td>541</td>
<td>0.403</td>
<td>44.09</td>
<td>20.59</td>
<td>4.82</td>
<td>1.7578</td>
<td>1.5711</td>
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<td>2</td>
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<td>538</td>
<td>0.393</td>
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<td>21.12</td>
<td>4.75</td>
<td>1.7134</td>
<td>1.4953</td>
</tr>
<tr>
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<td>552</td>
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<td>44.17</td>
<td>20.21</td>
<td>4.82</td>
<td>1.7911</td>
<td>1.6920</td>
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<tr>
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<td>539</td>
<td>0.373</td>
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<td>22.33</td>
<td>5.01</td>
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<td>1.3372</td>
</tr>
<tr>
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<td>21.48</td>
<td>5.11</td>
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<td>1.4389</td>
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<tr>
<td>B</td>
<td>8.124</td>
<td>536</td>
<td>0.334</td>
<td>44.2697</td>
<td>25.05</td>
<td>8.25</td>
<td>1.4450</td>
<td>1.0649</td>
</tr>
</tbody>
</table>
Preparation, Characterization and Electrochemical Performance of $\text{LiNi}_{x}\text{Co}_{y}\text{Cu}_{z}\text{Mn}_{2-x-y-z}\text{O}_4$ as Positive Electrodes in Lithium Rechargeable Batteries / J. New Mat. Electrochem. Systems

The AC impedance measurement amplitude was 50 mV. The frequency range was $10^5$–$10^{-2}$ Hz. The cells were charged and discharged at 0.020 A·cm$^{-2}$ between 2.5 and 4.5 V at room temperature.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization

X-ray diffraction (XRD) patterns of the six samples beside $\text{LiMn}_2\text{O}_4$ (sample A) and $\text{LiCo}_{0.25}\text{Cu}_{0.25}\text{Ni}_{0.25}\text{Mn}_{1.25}\text{O}_4$ (sample B) are shown in Fig. 1. The pattern of the $\text{LiMn}_2\text{O}_4$ sample has the distinct peaks reported in the literature [26]. Also, the other samples show mainly the same characteristic peaks. The as-prepared powders have spinel-phase cubic structure with space group Fd3m [27]. The unit cell lattice parameter, the crystallite grain size ($L$) using Scherer’s equation, and the dislocation densities of the crystal particles are given in Table 1. It can be observed that the crystallite size and surface area increase with the doping substitution of one, two, and three transition metals, respectively. The lattice constant, $a$, also decreases with the introduction of more than one metallic doping substitution. This occurs especially with Co and Ni metallic substitution. However, Cu doping causes little change in the unit cell dimension and consequently the crystallite size. This is attributed to the difference in ionic radii between manganese, which is larger in the octahedral coordination, and the various dopant ions. Similar observations for these dopant metals (Co, Ni, and Cu) have been reported in the literature [28, 29]. Furthermore, the strain, $\varepsilon$,
and the dislocation density, δ, of the crystals for the samples are given by the following formulas [30]:

\[ \varepsilon = -\beta \cos \theta / 4 \]  
\[ \delta = 15 \beta \cos \theta / 4aL \]

Where β is the full width half maximum (FWHM) according to the Scherer formula. It should be noted that the ε and δ values decrease with the use of more than one doping substitution.

This behavior can be explained as due to the more even arrangement and denser packing of the atoms in the crystal lattice structure, which decreases the lattice imperfections.

### 3.2. Morphological characterization

The morphology of the powders was observed with a scanning electron microscope (SEM) as shown in Fig. 2 for the eight samples. The SEM image of the multi-doped powder sample is quite different from that of the LiMn2O4. The morphology of the multi-doped crystals has a fine structure and small crystal size. Also, the crystal particles are shaped into spherical structures. Furthermore, the crystal particles are shaped into spherical structures. On the other hand, in the morphology of the six numbered samples, those with single rock structure and large crystalline particles. On the other hand, in comparison with samples 4-6, which contain two element doping. The average particle size from the SEM morphology is about 5 μm for sample A, while samples 1-3 have particles about 2 μm in size. On the other hand, samples 4-6 containing two doping elements show an average particle size of about 300 nm. Furthermore, sample B has an average particle size of about 250 nm. Also, the active surface area of the LiCo0.25Cu0.25Ni0.25Mn1.25O4 (sample B) is larger than that of the LiMn2O4 and the other six samples as observed in Table 1.

### 3.3. Electron paramagnetic resonance investigation

The electron paramagnetic resonance (EPR) spectra of the spinel LiMn2O4 (sample A) and the multi-doped compound (sample B) are shown in Fig. 3 (a-b). The data obtained for EPR signal of sample A consists of Lorentzian lines with parallel g-factor, \( g_\parallel = 1.55 \) and perpendicular g-factor, \( g_\perp = 2.7 \). The EPR line shows a significant broadening. The Mn4+-Mn3+ dipolar interactions as well as the Mn3+-Mn3+ ones contribute to the broadening of the signal. Most probably, this signal should be attributed to Mn3+ ions in a low symmetry crystal field. The difference in the magnetic field \( \Delta H = 2500 \) G. Also, the broadening effect of Mn3+ on the Mn4+ line width is due to the antiferromagnetic interactions. These results are in good agreement with reported ones in the work of Stoyanova et. al. [32, 33]. On the other hand, the data obtained for EPR spectrum of sample B, as illustrated in Fig. 3(b) consists of narrow Lorentzian lines with \( g_\parallel = 1.91 \) and \( g_\perp = 2.08 \). The difference in the magnetic field is only 300 G. Therefore, compound B is considered more magnetic than A. It was reported that the ESR spectrum of LiNi0.3Li0.7Mn2O4 showed a much narrower signal (\( \Delta H = 170 \) mT) centered at \( g = 2.0 \). The band has a complex shape with two components. The signal is attributed to Mn3+ ions, which are the only paramagnetic entities in this compound [34]. The main signal (the narrower one), ascribable to antiferromagnetically coupled Mn4+ ions in a Co3+-Mn4+-environment, possesses a Lorentzian line shape, with a g-factor of 2.004. The decrease in \( \Delta H \) gives evidence of an increase in the rigidity of the lattice with decreasing concentration of the Jahn–Teller Mn3+ ions and this lattice distortion experienced by the Mn4+ ions enhances the electrochemical properties [34].

### 3.4. Magnetic characterization

The temperature dependence of the magnetic susceptibility as a function of temperature for the above specimen samples is shown in Fig. 4. It was found that the low-temperature magnetic susceptibility increased with an increase in the substitution degree from one transition metal to three ones, indicating that the dominant magnetic coupling is converted from an antiferromagnetic to ferromagnetic one. i.e. the Mn4+-O2–Mn4+ ferromagnetic coupling increases and the antiferromagnetic Mn3+-O2–Mn3+ and Mn3+-O2–Mn4+ pairs are reduced [35]. This causes the shift of the Weiss temperature to the higher value (less negative). \( \chi_m \) is given by the following equation:

\[ \chi_m = C_p / (T - \theta_p) \]

where \( C_p \) is the Curie constant and \( \theta_p \) is the Weiss temperature.

Furthermore, it is found that the Curie constant \( C_p \) decreases with the more metal doping as recorded in Table 2. Also, the experimental effective magnetic moment \( \mu_{\text{eff}} \) can be found using the following formula [36-38]:

Table 2. the values of magnetic parameters for A, B and the six samples.

<table>
<thead>
<tr>
<th>Sample (S)</th>
<th>( C_p ) [emu.K/mole]</th>
<th>( \theta_p ) [K]</th>
<th>( \mu_{\text{eff}} ) [μB]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn2O4 (A)</td>
<td>4.5</td>
<td>-315</td>
<td>6.02455</td>
</tr>
<tr>
<td>LiCu0.25Mn1.25O4 (3)</td>
<td>4.326923</td>
<td>-281.25</td>
<td>5.90755</td>
</tr>
<tr>
<td>LiCo0.25Ni0.75Mn1.25O4 (2)</td>
<td>4.245283</td>
<td>-254.717</td>
<td>5.85156</td>
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<tr>
<td>LiNi0.25Mn1.25O4 (1)</td>
<td>4.16667</td>
<td>-233.09</td>
<td>5.797126</td>
</tr>
<tr>
<td>LiCo0.25Cu0.25Ni0.25Mn1.25O4 (6)</td>
<td>4.13679</td>
<td>-170.39</td>
<td>5.776304</td>
</tr>
<tr>
<td>LiNi0.3Li0.7Mn2O4 (5)</td>
<td>4.090909</td>
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<tr>
<td>LiNi0.3Li0.7Mn2O4 (4)</td>
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<td>5.593654</td>
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<tr>
<td>LiCo0.25Cu0.25Ni0.25Mn1.25O4 (B)</td>
<td>3.813559</td>
<td>-20.6695</td>
<td>5.546048</td>
</tr>
</tbody>
</table>
$\mu_{\text{eff}} = \mu_B \sqrt{\frac{3k_B C_P}{N_A}} = 2.84 \mu_B \sqrt{C_P}$  \hspace{1cm} (4)

where: $\mu_B$ is the Bohr magneton, $k_B$ is Boltzmann’s constant, and $N_A$ is Avogadro’s number. The values of the $\mu_{\text{eff}}$, $C_p$, and $\theta_p$ parameters are given in Table 2. The effective magnetic moment decreases with the more metal doping. The decreasing of $C_p$ and $\mu_{\text{eff}}$ means that the spin decreases from $S=2$ for Mn$^{3+}$ to $1.5$ for Mn$^{4+}$. Consequently, the oxidation of Mn ion in spinel compounds increases from A to B materials. In the Ni$^{2+}$, Co$^{3+}$ and Cu$^{2+}$-substituted case, the magnetic dilution is not expected, some new couplings (Mn$^{3+}$–O$^2$–Ni$^{2+}$, Mn$^{4+}$–O$^2$–Co$^{3+}$, Mn$^{4+}$–O$^2$–Cu$^{2+}$, Co$^{3+}$–O$^2$–Co$^{3+}$, Cu$^{2+}$–O$^2$–Cu$^{2+}$ and Ni$^{2+}$–O$^2$–Ni$^{2+}$) are introduced, and Ni$^{2+}$–O$^2$–Ni$^{2+}$ coupling is strong ferromagnetic one [39]. Subsequently, the compositional variation of the Curie constant becomes lower and the ferromagnetic Curie temperature attained at the compound having three doping metals takes a higher value (less negative) indicating the increasing of ferromagnetic interactions [36].

Both EPR and magnetic susceptibility measurements permit the differentiation of regions rich in lithium and manganese. The lithium–manganese distribution is of significant importance for understanding and correspondingly, for improving the electrochemical properties of LiMn$_2$O$_4$ and the other doped spinel compounds.

Furthermore, the increase of Mn$^{4+}$ and decrease of Mn$^{3+}$ ions concentration in sample “B” rather than the other samples as explained by the difference in the magnetic field “$\Delta H$” and the magnetic parameters $C_p$ and $\theta_p$, reduces the Jahn–Teller distortion of spinel LiCo$_{0.25}$Cu$_{0.25}$Ni$_{0.25}$Mn$_{1.25}$O$_4$ (sample B) in greater amount more than the other investigated samples. Similar results were obtained for LiNi$_{0.37}$Mn$_{1.5}$O$_4$, LiNi$_{1.5}$Mn$_{3.5}$O$_4$ and LiMg$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$ [40, 41]. It was explained for these mentioned spinel materials that the disordered phase present Mn$^{3+}$ ions in the structure, whereas in the ordered phase only Mn$^{4+}$ and Ni$^{2+}$ ions.

### 3.5. Electrochemical studies

Fig. 5 shows the electrochemical impedance spectra (EIS) of the cells. The intercept at high frequency on the real axis $Z'$ is for the resistance of the electrolyte, $R_e$, and this is followed by a semicircle in the high-middle frequency region and a straight line in the low frequency region. The numerical value of the diameter of the semicircle on the $Z'_\text{real}$ axis is approximately equal to the charge transfer resistance, $R_\text{ct}$. The values of $R_e$ and $R_\text{ct}$ are given in Table 3. The straight line in the low frequency region is attributed to the diffusion of the lithium ions into the bulk of the electrode material, the so-called Warburg diffusion. The plot of $Z_{\text{real}}$ versus the inverse square root of the angular frequency for the lower angular frequencies is presented in Fig. 6. The parameters of the impedance spectra

Table 3 Electrochemical impedance parameters of the cells prepared from A, B and the six samples.

<table>
<thead>
<tr>
<th>S</th>
<th>$R_e$</th>
<th>$R_\text{ct}$ [Ω]</th>
<th>$\sigma$ [Ωs$^{-1}$]</th>
<th>$D$ [cm$^2$s$^{-1}$]</th>
<th>$i$ [mAcm$^{-2}$]</th>
<th>$C_d$ [F]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25.97</td>
<td>409</td>
<td>819.01</td>
<td>5.27E-14</td>
<td>6.27E-05</td>
<td>4.02E-07</td>
</tr>
<tr>
<td>B</td>
<td>21.23</td>
<td>78</td>
<td>122.09</td>
<td>2.37E-12</td>
<td>3.29E-04</td>
<td>1.16E-06</td>
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<tr>
<td>1</td>
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<tr>
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<tr>
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</tr>
<tr>
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<td>185.24</td>
<td>1.03E-12</td>
<td>2.36E-04</td>
<td>9.59E-07</td>
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</table>
are listed in Table 3. The straight lines are attributed to the diffusion of the lithium ions into the bulk of the electrode materials, the so-called Warburg diffusion [42]. This relation is governed by equation (6) below. It is observed that the non-geometric Warburg impedance coefficient ($\sigma_w$) is 122.09 W s$^{-0.5}$ for sample B, which is lower than the value for sample A (819.01 $\Omega$ s$^{-0.5}$). In addition, the diffusion coefficient values of the lithium ions diffusing into the bulk electrode materials were calculated using Equation (7) and are listed in Table 3. Sample B has a higher $D$ value than sample A for Li$^+$ ions.

$$Z_{re} = R_e + R_{ct} + \sigma_w \cdot \omega^{0.5}$$

$$D = 0.5 \left( \frac{RT}{A n^2 F^2 \sigma_w C} \right)^2$$

$$Z_{re} = R_e + R_{ct} + 2\sigma_w^2 \cdot C_{dl}$$

Where $\omega$ angular frequency in the low frequency region, $D$: diffusion coefficient, $R$: the gas constant, $T$: the absolute temperature, $F$: Faraday’s constant, $A$: the area of the electrode surface, $C_{dl}$: double layer capacitance of the working electrode, and $C$: molar concentration of Li$^+$ ions. In addition, the angular frequency is given by:

$$\omega = \frac{1}{R_{ct} \cdot C_{dl}}.$$  

Furthermore, the exchange current density ($i^\circ = RT/nF R_{ct}$) and the double layer capacitance ($C_{dl}$) values of the doped sample B are higher than for sample A using equations (8) and (9). Therefore, the charge-transfer reaction in the doped spinel sample electrode takes place faster than in the electrode containing the undoped material. On the other hand, the other samples (1-6) show impedance parameters that lie between those of samples A and B. Also, the impedance parameters with two doping elements are better than the parameters with one doping in Table 3.

### 3.5.1. Reduction process

Two peaks at 3.9 and 4.12 V for the intercalation of two Li$^+$ ions into the spinel phase, as explained by equations (9) and (10).

$$\lambda$-MnO$_2$ + Li$^+$ \rightarrow LiMn$_2$O$_4$ \quad E = 4.1 \text{ V}$$

The first charge - discharge capacity plateaus versus the working voltage are shown in Fig. 7. Similar results were reported [8, 41]. The first cyclic voltammogram of LiMn$_2$O$_4$ starts from the open circuit potential (OCP) at 3.1 V for cells A and B, respectively as shown in Fig. 8 (a-b).

**Figure 6.** Relationship between real impedance ($Z'$) and angular frequency for LiMn$_2$O$_4$ (A), LiNi$_{0.75}$Mn$_{1.25}$O$_4$ (1), LiCo$_{0.75}$Mn$_{1.25}$O$_4$ (2), LiCu$_{0.75}$Mn$_{1.25}$O$_4$ (3), LiNi$_{0.37}$Co$_{0.37}$Mn$_{1.25}$O$_4$ (4), LiNi$_{0.37}$Cu$_{0.37}$Mn$_{1.25}$O$_4$ (5), LiCo$_{0.37}$Cu$_{0.37}$Mn$_{1.25}$O$_4$ (6), and Li-Co$_{0.25}$Cu$_{0.25}$Ni$_{0.25}$Mn$_{1.25}$O$_4$ (B) cells.

**Figure 7.** The potential vs. first specific discharge capacity profiles for LiMn$_2$O$_4$ (A), (1-6) and Li-Co$_{0.25}$Cu$_{0.25}$Ni$_{0.25}$Mn$_{1.25}$O$_4$ (B) cells.

**Figure 8.** Cyclic voltammograms of spinel compounds LiMn$_2$O$_4$ (a) and Li-Co$_{0.25}$Cu$_{0.25}$Ni$_{0.25}$Mn$_{1.25}$O$_4$ (b). The scan rate is 0.1 mVs$^{-1}$. 
V, which expresses the reduction of Ni $^{4+}$ to Ni $^{2+}$, Co $^{3+}$ to Co $^{2+}$, of Mn$^{3+}$ to Mn$^{2+}$, which takes place through the intercalation of one dopant for Mn ions in LiMn$_2$O$_4$ gives rise to a 5 V potential plateau, while the kind of substitution ion influences the 5 V behavior of Li$_{1-x}$Mn$_{2-2x}$O$_4$ (Me = Cr, Fe, Co, Ni, Cu) cathode materials [20, 44]. It was reported that the oxidation of Ni$^{2+}$ to Ni$^{3+}$ and Ni$^{3+}$ gives higher potential such as 5 V behavior [41]. From the energy levels of the d-orbitals in Mn and Ni ions, it can be expected that a 4 V potential plateau corresponds to the redox couple of Mn$^{3+}$/Mn$^{4+}$, while the ones at 5 V are due to two redox couples of Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$. The discharge curve at 5 V involves two plateaus. The lower potential plateau is assigned to the Ni$^{3+}$/Ni$^{4+}$ redox couple, and the higher one is contributed by the Ni$^{2+}$/Ni$^{3+}$ redox couple. Also, the redox couples of Co$^{3+}$/Co$^{4+}$ and Co$^{2+}$/Co$^{3+}$ possess 5 V potentials that are in agreement with a previous reported work [41].

The cycle life performances of the numbered samples from 1 to 6, A and B are presented in Fig. 9. It shows that the multi-doped spinel material has higher discharge capacity of 150 mAh$^{-1}$ compared to 125 mAh$^{-1}$ for the spinel LiMn$_2$O$_4$ after 150 cycles. The discharge capacity of the multi-doped sample B is larger by about 15 % than that of the un-doped sample A. Also, it is observed that the six numbered samples have specific discharge capacities that lie between the multi-doped and un-doped samples. Mohamedi et al. [46] mentioned that the electrode initially delivered a capacity of 155 mAh g$^{-1}$, which is very close to the theoretical capacity of 150 mAh g$^{-1}$, when all lithium can be extracted from LiNi$_{0.5}$Mn$_{1.5}$O$_4$. Leroux and Nazar [47] showed a specific capacity of 160 mAh g$^{-1}$ at C/1.8 (85 mA g$^{-1}$) for Li$_{0.5}$K$_{0.0}$MnO$_4$. Zhang et al. [48] showed the first charge capacity and discharge capacity are 184 and 172 mAh$^{-1}$ for LiNi$_{1.3}$Mn$_{1.3}$Co$_{0.3}$, respectively.

4. CONCLUSION

We have studied the structural, physical, and electrochemical properties of Ni, Cu and Co-substituted Li$_{1-x}$Ni$_x$Mn$_{2-2x}$O$_4$ positive electrode materials synthesized by a sol–gel method from ammonia and glycine precursors. X-ray diffraction patterns, SEM, and magnetic measurements were carried out. XRD patterns have shown spinel-phase cubic structure with space group Fd3m. The magnetic susceptibilities, Curie constant, Weiss temperature and the effective magnetic moment increase with the more metal doping. The voltage profiles of the spinel oxide samples monitored against lithium electrode show that the overall capacity of positive electrodes was about 155 mAh g$^{-1}$ for cell B, while it was 115 mAh g$^{-1}$ for cell A. However, more stable charge–discharge cycling performances have been observed with more than 150 mAh g$^{-1}$ when electrodes are charged up to 4.5 V for cell B as compared to the performances of the native oxide cell A.

REFERENCES

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