THE APPLICATION OF LiMn$_2$O$_4$ SYNTHESIZED FROM MANGANESE ORE FOR LITHIUM-ION BATTERIES CATHODE

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ABSTRACT
Lithium manganese oxide (LiMn$_2$O$_4$) synthesized from manganese ore has been successfully applied for cathode materials of lithium-ion batteries. LiMn$_2$O$_4$ was obtained by reacting lithium carbonate (Li$_2$CO$_3$) and manganese oxide (MnO$_2$) using a solid-state reaction. The structure characterization of LiMn$_2$O$_4$ was carried out using X-ray diffraction (XRD) and Raman spectroscopy. The thermal properties of cathode material were studied using Thermal Gravimetric Analysis (TGA). The electrochemical properties were analyzed using cyclic voltammetry (CV), charge-discharge (CD), and Electrochemical Impedance Spectroscopy (EIS). Two pairs of redox peaks were identified at 3.0-4.5 V. The efficiency of the battery was 94.74% in the first cycle with maximum electrical conductivity of 5.26 x 10$^{-1}$ S cm$^{-1}$. It was concluded that LiMn$_2$O$_4$ synthesized from manganese ore can be applied as the cathode of lithium-ion batteries.

Keywords: Manganese Ore, Lithium-ion Batteries, Cathode Material, Conductivity.

INTRODUCTION
Lithium-ion batteries (LIBs) were the most widely energy storage used for portable electronic devices and many other industrial applications.$^{1-4}$ LIBs were widely used because of their high energy density, long life cycles, and excellent storage capacity.$^5$ At the beginning of the 1970s, lithium batteries based on Li/Li$^+$ were introduced. Then, Sony Corporation (Japan) commercialized lithium-ion batteries (Li$_x$C$_6$/Li$^+$/Li$_2$CoO$_2$) in the 1990s.$^1,6$ Lithium cobalt oxide (LiCoO$_2$) was commercial cathode material that has high storage capacity (170 mA h g$^{-1}$) and working potential (3.93 V vs Li/Li$^+$), but it has some disadvantages in terms of its toxicity, supply difficulties, and relatively expensive.$^7$ Recently, lithium manganese oxide (LiMn$_2$O$_4$) has attracted a lot of attention as a potential cathode material because it was nontoxic, more abundant, low-cost high energy density, and has high thermal stability.$^{3,4,8,9}$ Manganese (Mn) was found in nature as a mineral like braunite (2Mn$_2$O$_3$, MnSiO$_3$), cryptomelane (KMn$_4$O$_8$), hausmannite (Mn$_3$O$_4$), manganese (Mn$_2$O$_3$,H$_2$O), pyrolusite (MnO$_2$), psilomelane (BaMn$_4$O$_8$,8H$_2$O)), rhodochrosite (MnCO$_3$), and rhodonite (MnSiO$_3$).$^{10}$ The estimated abundance of Mn in the Earth’s crust was 0.095%$^{11}$. Manganese ore (MnO$_2$) can be found in several regions in Indonesia.$^{12}$ Previously, Kang et al., 2014 reported that MnO$_2$ can be used as cathode materials (LiMn$_2$O$_4$) in LIBs. MnO$_2$ and its composites have been used in battery applications because of their natural abundance, low-cost processing, environmentally friendly, high porosity, and high voltage.$^{13}$ MnO$_2$ has a variety of polymorphs ($\alpha$, $\beta$, $\gamma$, $\lambda$, $\delta$-) and various morphologies such as nanowires, nanospheres, nanosheets, or nanorods, which influence its conductivity so it can be applied as cathode materials in LIBs.$^{14,15}$ In this research, the synthesis of LiMn$_2$O$_4$ cathode materials was carried out by reacting lithium carbonate (Li$_2$CO$_3$) as a Li source and manganese oxide (MnO$_2$) extracted from manganese ore as an Mn source by solid-state reaction. The solid structure and thermal properties of LiMn$_2$O$_4$ cathode materials that were obtained were characterized using XRD, Raman spectroscopy, and TGA. The cathode materials were assembled into CR2032 lithium batteries in half coin cells and the electrochemical performance was evaluated using CV, CD, and EIS to analyze the
electrochemical reaction, charge capacity, and materials conductivity, respectively. Eventually, the potential applications for lithium-ion battery cathode were evaluated.

EXPERIMENTAL

Material and methods
Preparation of LiMn$_2$O$_4$
The manganese ore (MnO$_2$) used in this study was obtained from Tulungagung, East Java, Indonesia. The MnO$_2$ preparation was done according to the previously reported method.$^{12}$ Figure-1 represents LiMn$_2$O$_4$ preparation. Briefly, Li$_2$CO$_3$ and MnO$_2$ were mixed with a Li and Mn ratio of 1:4. The mixtures were calcined at 750 °C for 4 hours and then sintered at 900 °C for 4 hours to produce LiMn$_2$O$_4$.

![Fig.-1: Schematic illustration for the Synthesis of LiMn$_2$O$_4$](image)

Structural Characterization
The structure of LiMn$_2$O$_4$ was characterized using XRD (PANalytical Xpert PRO) at the 2θ ranges from 5° to 90°, 40 kV, and 30 mA with Cu-Kα$_1$ (λ = 1.54060 Å) and Raman spectroscopy (Horiba Scientific, Japan) with 532 nm lasers and 100x magnification. TGA (Mettler Toledo, USA) was used to evaluate the thermal decomposition of LiMn$_2$O$_4$ from room temperature to 1000 °C with a heating rate of 10°C/min.

Coin Cell Assembly
The battery's electrode slurry was prepared from LiMn$_2$O$_4$ as active material, polyvinylidene fluoride (PVDF) as the binder, and Super P$^{TM}$ as a conductive material, in a ratio of 8:1:1, respectively, in N, N-dimethylacetamide solvent. The slurry was coated on aluminum foil using a “doctor blade” to obtain the cathode film. The cathode film was dried in a dry box at 80°C for 1 hour and placed in an oven for 24 hours. The cathode film was broken into 16 mm in diameter disks. The CR2032 lithium battery half coin cell was assembled in the glove box with an argon atmosphere. The components of the coin cell were the positive case, cathode film (LiMn$_2$O$_4$), separator (polyvinyl alcohol (PVA)), electrolyte (lithium hexafluorophosphate (LiPF$_6$)), anode (lithium metal), spacer, spring, and negative case. The composition of electrolyte that was applied was 1 M LiPF$_6$ that dissolved in ethylene carbonate (EC): dimethyl carbonate (DMC) with a ratio of (1:6). All of the coin cell components were crimped in the glove box.

Electrochemical Evaluation
The CV and CD of the half coin cells were performed using Automatic Battery Cycler (WonAtech WBCS3000, Korea). The scan rate of CV was set at 0.1 mVs$^{-1}$ with an applied voltage of 3.0-4.5V. The charge-discharge capacity rate was 0.1 C. The characterization using EIS (Autolab PGSTAT 128N) was carried out at frequency ranges of 0.01 Hz – 100 kHz with an amplitude of 5 mV.

RESULTS AND DISCUSSION

Structural Characterization
Figure-2(a) shows the XRD patterns of initial manganese ore with pyrolusite (MnO$_2$) as the main composition. The diffraction peaks at 2θ: 28.64° (110), 42.73° (111), and 56.74° (211) represent the diffraction of β-MnO$_2$ (JCPDS standard No. 24-0735).$^{16–18}$ Figure-2(b) shows the XRD patterns of LiMn$_2$O$_4$, the peaks at 2θ of 18.63° (111), 36.12° (311), 37.79° (222), 43.93° (400), 48.11° (313), 58.07° (333), 63.84° (404), and 67.29° (531) confirm that LiMn$_2$O$_4$ has been successfully synthesized (match with JCPDS standard No. 35-0782).$^{19,20,4,21}$ In addition, LiMn$_2$O$_4$ has a cubic spinel phase with an Fd3m space group, in which lithium ions occupy the 8a sites (tetrahedral), manganese ions locate in the 16d sites (octahedral), and oxygen ions position in the 32e sites.$^{1,22,23}$
Figure-3 shows Raman spectra for MnO$_2$ and LiMn$_2$O$_4$. Raman scattering gives structural information at the atomic scale of MnO$_2$ and LiMn$_2$O$_4$ via vibrational technique. In general, Raman spectra of Mn-O were distinguished into three major regions such as the skeletal vibration at 200-450 cm$^{-1}$, the deformation modes of the Mn-O-Mn chain in the octahedral lattice at 450-550 cm$^{-1}$, and the stretching modes of Mn-O bonds in the MnO$_6$ octahedral at 550-750 cm$^{-1}$.

Furthermore, Raman spectroscopy of LiMn$_2$O$_4$ found several spectral regions in the range of 100-800 cm$^{-1}$ (strong bands around 625 cm$^{-1}$ and weak bands in the range of 200-500 cm$^{-1}$). This strong Raman signal was due to the Mn-O vibration at 625 cm$^{-1}$. The previous study reported that the vibration from Mn-O was divided into two types i.e. isotropic vibration from the octahedral Mn$^{4+}$O$_6$ and distortion Mn$^{3+}$O$_6$.$^{25,26}$ Figure-3(b) shows the strong band at 624 cm$^{-1}$ which can be identified as stretching symmetric vibration in the Mn-O octahedral bonds. The shoulder at 580 cm$^{-1}$ was predicted as manganese's average oxidation state in the spinel phase. The band with medium intensity was located at 502 cm$^{-1}$ and the band with lower intensity occurs at 463 cm$^{-1}$. Julien et al., 2006 reported that the Mn$^{3+}$ and Mn$^{4+}$ cations were equivalent with crystallography (16d sites) in XRD data.$^{25}$ Figure-4 shows the TGA analysis of MnO$_2$ and LiMn$_2$O$_4$. The TGA curve of MnO$_2$ (Fig.-4(a)) describes that there were several steps of weight loss. In the first step, a small amount of weight lost at 200°C was identified as water evaporation. In the next step, 10.6% of weight loss observed at 500°C to 600°C came from the decomposition of MnO$_2$ to Mn$_2$O$_3$. Then, 1.9% of weight lost at 750°C to 860°C was the transformation of Mn$_2$O$_3$ to Mn$_3$O$_4$. The weight loss resembled the release of oxygen as a result of the MnO$_2$ reduction. The reactions that occur were represented in equations (1) and (2)$^{27-30}$:

$$2 \text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + \frac{1}{2} \text{O}_2 \quad (1)$$

$$3 \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 + \frac{1}{2} \text{O}_2 \quad (2)$$
The TGA curve shows that the sample (MnO$_2$) reaches stability at a temperature higher than 860 °C as there was no further weight loss observed. This indicates that the decomposition of MnO$_2$ was completed. Figure-4(b) shows the TGA curve of LiMn$_2$O$_4$, which shows a small weight loss, 5.5% between 750°C and 870°C. The decomposition of LiMn$_2$O$_4$ occurred at above 750°C related to the liberation and volatilization of lithium at high temperatures. After the temperature reaches 900 °C, the sample (LiMn$_2$O$_4$) decomposition was completed. These results were in accordance with the TGA curve of LiMn$_2$O$_4$ reported by Hashem et al., 2019.

![TGA Curve of (a) MnO$_2$ and (b) LiMn$_2$O$_4$](image)

**Electrochemical Properties**

The electrochemical properties of Li$^+$ insertion/extraction in LiMn$_2$O$_4$ were evaluated using CV analysis. The CV analysis of LiMn$_2$O$_4$ cathode material in the lithium-ion battery was reported. In this study, the cyclic test was carried out at voltage ranges 3.0-4.5 V with a scan rate of 0.1 mVs$^{-1}$.

![Cyclic Voltammograms of LiMn$_2$O$_4$ during the 1$^{st}$ and 3$^{rd}$ Cycle](image)

Figure-5 showed that CV curves have two pairs of reversible redox peaks where the position of anode peaks ($E_{pa1}$, $E_{pa2}$) and cathode peaks ($E_{pc1}$, $E_{pc2}$) were shown in Table-1. The first peaks ($E_{pa1}$ and $E_{pc1}$) indicated the extraction/insertion process of Li$^+$ between LiMn$_2$O$_4$/LiMn$_{0.5}$O$_4$. The second peaks ($E_{pa2}$ and $E_{pc2}$) were the extraction/insertion process of Li$^+$ between LiMn$_{0.5}$O$_4$/MnO$_2$. The two pairs of redox peaks were typical of the stoichiometric spinel phase where both processes of moving Li$^+$ on half of the tetrahedral 8a sites was lead to Mn$^{3+}$/Mn$^{4+}$ redox reaction. Based on Fig.-5 and Table-1, it can be seen that during the 1$^{st}$ and 3$^{rd}$ cycles peak patterns were similar, and potential distinctions were very small.

Figure-6 shows the charge-discharge curve of LiMn$_2$O$_4$ at 1$^{st}$ and 3$^{rd}$ cycles under a current density of 0.1 C in the voltage ranges of 3.0-4.5 V. The charge-discharge profiles represent two distinct plateaus, which describe different processes from Li$^+$ insertion/extraction. The charging process was the intercalation of Li$^+$ toward the anode host, whereas the discharging process was the de-intercalation of Li$^+$ back to the cathode.
host. The charging process starts when the coin cell was supplied with a voltage input of 3V, where Li$^+$ begins to move from the cathode to electrolyte media through the separator and anode until the maximum condition was achieved. The maximum condition occurs when all Li$^+$ were migrated to the anode at 4.5V.$^{32}$

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Potential Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{pa1}$</td>
</tr>
<tr>
<td>1st</td>
<td>4.13</td>
</tr>
<tr>
<td>3rd</td>
<td>4.12</td>
</tr>
</tbody>
</table>

Fig.-5: The 1st and 3rd Charge-Discharge Curves of LiMn$_2$O$_4$

Table-2 shows the charge-discharge capacity and coulomb efficiency of the sample. The charge-discharge specific capacity of LiMn$_2$O$_4$ was 148 mAh/g.$^6$ The LiMn$_2$O$_4$ synthesized MnO$_2$ in this research has to be optimized to obtain better capacity, although it has good charge efficiency (close to 100%). This low capacity could be caused by the presence of impurity from raw materials interfering intercalation/de-intercalation process of Li. The Coulombic efficiency, 94.74 % at the 1st cycle, indicated the energy cycles during the charge-discharge process.

Table-2: Capacity and Coulomb Efficiency of LiMn$_2$O$_4$

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Capacity</th>
<th>Coulomb Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Charge (mAh/g)</td>
<td>Discharge (mAh/g)</td>
</tr>
<tr>
<td>1st</td>
<td>58.90</td>
<td>55.80</td>
</tr>
<tr>
<td>3rd</td>
<td>57.10</td>
<td>56.50</td>
</tr>
</tbody>
</table>

Fig.-6: Nyquist Plots of LiMn$_2$O$_4$ after 1st and 3rd Cycle

The variation of LiMn$_2$O$_4$ electrode resistance was investigated using EIS, at 0.01 Hz-100 kHz with an amplitude of 5 mV. Figure-7 represents the Nyquist plots of LiMn$_2$O$_4$ after the 1st and 3rd charge-discharge
cycles. The electrolyte resistance ($R_e$) was intercepted at the real ($Z'$) axis in high frequency and the charge transfer resistance ($R_{ct}$) was semicircle in the middle-frequency range.\textsuperscript{34}

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$R_e$ ($\Omega$)</th>
<th>$R_{ct}$ ($\Omega$)</th>
<th>$\sigma_e$ (S cm\textsuperscript{-1})</th>
<th>$\sigma_{ct}$ (S cm\textsuperscript{-1})</th>
<th>$\sigma_{total}$ (S cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st}</td>
<td>14.51</td>
<td>21.43</td>
<td>3.14 x 10\textsuperscript{-4}</td>
<td>2.13 x 10\textsuperscript{-4}</td>
<td>5.26 x 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>3\textsuperscript{rd}</td>
<td>15.04</td>
<td>23.29</td>
<td>3.03 x 10\textsuperscript{-4}</td>
<td>1.95 x 10\textsuperscript{-4}</td>
<td>4.98 x 10\textsuperscript{-4}</td>
</tr>
</tbody>
</table>

The electrical conductivity ($\sigma_{total}$) of the LiMn$_2$O$_4$ sample was determined using equations 3 and 4\textsuperscript{34}:

\[
\sigma_{total} = \sigma_e + \sigma_{ct}
\]

\[
\sigma = \frac{t}{A\times R}
\]

Where $\sigma_e$ was the calculated electrolyte conductivity and $\sigma_{ct}$ was the calculated charge transfer conductivity in S cm\textsuperscript{-1}, $t$ is the film thickness, $A$ was the cross-sectional area, and $R$ was the resistance in $\Omega$. The resistance and conductivity values were shown in Table-3, with film thickness ($t$) of 0.0092 cm and cross-sectional area ($A$) of 2.0206 cm\textsuperscript{2}. Table-3 showed that the highest electrical conductivity was 5.26 x 10\textsuperscript{-4} S cm\textsuperscript{-1} in the first cycle of the EIS test, then a little decrease was observed in the third cycle. This indicates that the LiMn$_2$O$_4$ performance will slowly decrease as the current and voltage were applied continuously.

**CONCLUSION**

The lithium manganese oxide (LiMn$_2$O$_4$) has been successfully synthesized from lithium carbonate (Li$_2$CO$_3$) and manganese ore (MnO$_2$) using a solid-state reaction method. LiMn$_2$O$_4$ can be used as cathode materials in the lithium-ion battery. The cathode materials have two pairs of reversible peaks between 3.0-4.5V. The charge-discharge capacities obtained were 58.90 and 55.80 mAh/g with a coulomb efficiency of 94.74%. The electrical conductivity in the first cycle was 5.26 x 10\textsuperscript{-4} S cm\textsuperscript{-1}.

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