Enhanced Energy Density of Li$_2$MnSiO$_4$/C Cathode Materials for Lithium-ion Batteries through Mn/Co Substitution

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ABSTRACT

The crystal structure, morphology, and galvanostatic cycling and rate performances of cobalt-substituted Li$_2$MnSiO$_4$/C compounds, Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C ($x = 0.25, 0.5, and 0.75$), were evaluated and compared with those of Li$_2$MnSiO$_4$/C and Li$_2$CoSiO$_4$/C. Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C ($x = 0.25, 0.5, and 0.75$) compositions comprising uniform nanosized primary particles and no impurities were successfully synthesized using a hydrothermal method, followed by carbon coating. In addition, Li$_2$MnSiO$_4$/C and Li$_2$CoSiO$_4$/C were synthesized for comparison. The synthesized Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C ($x = 0.25, 0.5, and 0.75$) were solid solutions and were identified using an orthorhombic unit cell with Pmn2$_1$ space group symmetry. Although the capacity fades for Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C, the discharge capacity, average discharge voltage and rate capability of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C increased more than those of Li$_2$MnSiO$_4$/C and Li$_2$CoSiO$_4$/C when Co was substituted for Fe. Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$/C exhibited the best electrochemical performance compared with Li$_2$MnSiO$_4$/C and Li$_2$CoSiO$_4$/C, which was greater than that of LiMn$_2$O$_4$ (500 Wh kg$^{-1}$) and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (600 Wh kg$^{-1}$). The good electrochemical performance of Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$/C is attributed to its lower charge transfer resistance relative to that of Li$_2$MnSiO$_4$/C.

Keywords : Lithium Manganese Orthosilicate, Hydrothermal, Cathode Material, Lithium-ion Batteries

1. Introduction

Lithium transition metal orthosilicates, Li$_2$MSiO$_4$ compounds (where M = Fe, Mn, Co, or Ni), are considered to be promising cathode materials for next-generation lithium-ion batteries because they can theoretically deliver high specific capacities (>300 mAh g$^{-1}$) owing to the reversible insertion/extraction of two lithium ions per formula unit. Moreover, Li$_2$MSiO$_4$ compounds having a polyanionic structure offer higher stability compared with conventional lithium transition metal oxides such as LiCoO$_2$, LiMn$_2$O$_4$, and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ because the oxygen ions are bound by strong covalent bonds.

Li$_2$MnSiO$_4$-based materials have been intensively studied as Li$_2$MnSiO$_4$ is expected to demonstrate a higher discharge capacity than Li$_2$FeSiO$_4$ and Li$_2$CoSiO$_4$, owing to the extraction of two lithium ions at lower potentials (4.1 and 4.5 V corresponding to the Mn$^{2+}$/Mn$^{4+}$ and Mn$^{3+}$/Mn$^{4+}$ redox couples, respectively). To improve the discharge capacity of Li$_2$MnSiO$_4$, many researchers have focused on cation doping, carbon coating, and reducing the particle size. On the other hand, the experimental energy density of Li$_2$MnSiO$_4$ is much less than the theoretical one owing to its lower average discharge voltage (~3 V).

One way to achieve higher discharge voltage of Li$_2$MnSiO$_4$ is to substitute Co for Mn (solid solution of Li$_2$MnSiO$_4$ and Li$_2$CoSiO$_4$) as Li$_2$CoSiO$_4$ exhibits a well-defined plateau around 4.25 V, which is at a level higher than that of Li$_2$MnSiO$_4$. Moreover, in our previous report, we showed that Li$_2$Fe$_{0.5}$Mn$_{0.5}$SiO$_4$ exhibits a higher discharge voltage with 10 mol.% substitution of Co for Fe and Mn (Li$_2$Fe$_{0.5}$Mn$_{0.5}$SiO$_4$ tie-line). Hence, it is interesting to investigate whether Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C exhibits improved electrochemical performance compared with Li$_2$MnSiO$_4$/C and Li$_2$CoSiO$_4$. In this study, we report the hydrothermal synthesis of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C ($x = 0.25, 0.50, and 0.75$) followed by carbon coating. In addition, Li$_2$MnSiO$_4$ and Li$_2$CoSiO$_4$ were synthesized for comparison. Furthermore, the crystal structure, morphology, and galvanostatic cycling and rate performances of these materials were investigated.

2. Experimental

2.1 Synthesis

The starting materials included LiOH·H$_2$O, MnSO$_4$·5H$_2$O (Kanto Chemical Co. Inc., special grade), CoSO$_4$·7H$_2$O (Wako Pure Chemical Ind. Ltd., special grade), and Na$_4$SiO$_4$·nH$_2$O (Wako Pure Chemical Ind. Ltd., SiO$_2$ = 20%–23%). Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C...
Constant voltage charge (charging continued at 4.5 V until the stoichiometric amounts of the reactants (LiOH·H₂O synthesized as follows. Precursor mixtures were prepared by mixing stoichiometric amounts of the reactants LiOH·H₂O with distilled water (30 ml) under a N₂ atmosphere to prevent oxidation of the transition metals (Mn²⁺ or Co²⁺). Each prepared precursor mixture was transferred to a 200 ml Teflon-lined stainless steel autoclave. The autoclave was then purged with N₂ gas, sealed, and heated at 150°C for 12 h while stirring. After completion of the hydrothermal reaction, the resulting mixture was filtered, washed with a 1 wt.% aqueous LiOH solution (100 ml), and then freeze-dried for 12 h. Subsequently, each dried powder (2.00 g) was mixed with glucose (0.50 g) and distilled water (3.0 ml) and then dried again at 80°C for 12 h in air, followed by annealing at 600°C in a H₂/Ar (2% H₂) atmosphere to achieve a carbon coating by the decomposition of the glucose.

2.2 Characterization

The crystalline phases of the samples were identified using powder X-ray diffraction (XRD) with a Bruker D8 ADVANCE diffractometer with CuKα (λ = 0.15406 nm) radiation operating at 35 kV and 350 mA. The XRD patterns were collected in the 2θ range from 10° to 55° using a scanning step length of 0.0234° and scanning speed of 0.13 sec/step. The lattice parameters were calculated using the Le Bail method and the TOPAS3.0 software (Bruker).

The particle morphology of the samples was observed using a field emission scanning electron microscope (FESEM, JEOL-7500F) employing a secondary electron image detector and a TESCAN VEGA 3 LMU electron microscope (HRTEM; JEOL-ARM200F) equipped with a 200 kV dispersive X-ray spectroscopy (EDS) systems employing a secondary electron image detector and a TESCAN VEGA 3 LMU electron microscope.

2.3 Electrochemical measurements

The electrochemical properties of the samples were examined using CR2032 coin-type cells. Composite electrodes were fabricated by mixing 75 wt.% active material, 20 wt.% Ketjen Black (Lion Corp., CarbonECP) as the conducting agent, and 5 wt.% polyvinylidene difluoride (Kureha Chemical Ind. Co., Ltd., KFP9100) as the binder, in N-methyl-2-pyrrolidone (Wako Pure Chemical Ind. Ltd., special grade). The prepared slurry was coated on an Al foil using an ARKADIA pint (Honjo Metal Corp.) as the counter electrode. The electrolyte solution comprised 1 M LiPF₆ in a 3:7 mixture of ethylene carbonate and ethyl methyl carbonate, respectively. The separators comprised porous polypropylene (Celgard 2400). The CR2032 coin-type cells were constructed in an argon-filled glove box (dew point < −90°C, O₂ level < 0.2 ppm).

Galvanostatic charge–discharge cycling was performed on the CR2032 coin-type cells at 30°C using a battery testing system (Hokuto-Denko Co., model: HJ1001SM8A). The cells were cycled in a voltage range of 1.5–4.5 V using a constant current plus constant voltage charge (charging continued at 4.5 V until the current reached a value corresponding to 1/10th of the value of the charging current rates for a constant current protocol) at current rates of 33, 165, and 330 mA g⁻¹. The discharge behavior was tested at 1.5 V using a constant current protocol at the same rates of charge. Electrochemical impedance spectroscopy (EIS) was performed on the CR2032 coin-type cells at the open circuit voltage using a VersaSTAT4 system (Princeton Applied Research Co.) over the frequency range of 0.01–100 kHz with a 5 mV rms AC signal at 30°C.

3. Results and Discussion

3.1 Chemical and physical properties

The crystal structure and morphology of the Li₂Mn₁–ₓCoₓSiO₄ (x = 0.25, 0.5, and 0.75), Li₂MnSiO₄, and Li₂CoSiO₄ samples were characterized and compared. Table 1 shows the chemical composition determined using ICP-AES and the carbon content for Li₂Mn₁–ₓCoₓSiO₄/C (x = 0.25, 0.5, and 0.75), Li₂MnSiO₄/C, and Li₂CoSiO₄/C. The chemical compositions of all samples were in good agreement with the expected ones. Furthermore, as shown in Table 1, the carbon content of all samples was determined to be approximately 4 wt.%.

Figure 2 shows the powder XRD patterns for Li₂Mn₁–ₓCoₓSiO₄ (x = 0.25, 0.5, and 0.75), Li₂MnSiO₄, and Li₂CoSiO₄. All observed diffraction lines were attributed to an orthorhombic unit cell with Pmm2₁ space group symmetry (JCPDS no. 24-0608 and ICSD no. 191543). As seen in Fig. 2, there was no evidence of impurity phases such as Li₂SiO₃, MnO or CoO₄, 24,27,31,32 On the

| Chemical composition | Carbon content (wt.%) |
|----------------------|----------------------|
| Li₂MnSiO₄            | 4.1                  |
| Li₂Mn₀.₇₅Co₀.₂₅SiO₄  | 4.1                  |
| Li₂Mn₀.₂₅Co₀.₇₅SiO₄  | 4.3                  |
| Li₂CoSiO₄            | 4.3                  |
| Li₂Mn₀.₂₅Co₀.₇₅SiO₄  | 4.3                  |
| Li₂Mn₀.₂₅Co₀.₇₅SiO₄  | 4.3                  |
| Li₂Mn₀.₂₅Co₀.₇₅SiO₄  | 4.3                  |
| Li₂Mn₀.₂₅Co₀.₇₅SiO₄  | 4.3                  |

Figure 2. Powder XRD patterns of (a) Li₂MnSiO₄, (b) Li₂Mn₀.₇₅Co₀.₂₅SiO₄, (c) Li₂Mn₀.₂₅Co₀.₇₅SiO₄, (d) Li₂Mn₀.₇₅Co₀.₂₅SiO₄, and (e) Li₂CoSiO₄.
other hand, the diffraction peaks at $2\theta = 16.5, 24.9,$ and $28.3^\circ$ decreased in intensity with increasing Co content in the Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$ composition. This may be attributed to cation mixing between Co and Li. Therefore, further studies are needed to identify this possible cation mixing process via neutron diffraction. Figure 3 shows the refinement patterns by Le Bail method for Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$ ($x = 0.25, 0.5,$ and $0.75$), Li$_2$MnSiO$_4$, and Li$_2$CoSiO$_4$. Table 2 lists the powder XRD data and the lattice parameters and crystallite sizes calculated using the Le Bail method. As seen in Fig. 3, all difference patterns between the experimentally observed and calculated ones were almost straight lines. These results indicate that all calculated patterns are in good agreement with the experimentally observed ones. The lattice parameters were $a = 6.3185(2)$ Å, $b = 5.3832(3)$ Å, and $c = 4.9736(2)$ Å for Li$_2$MnSiO$_4$ and $a = 6.2647(1)$ Å, $b = 5.3720(10)$ Å, and $c = 4.9245(1)$ Å for Li$_2$CoSiO$_4$. These values were consistent with those previously reported by Li et al. ($a = 6.308$ Å, $b = 5.377$ Å, and $c = 4.988$ Å) and Gong et al. ($a = 6.267$ Å, $b = 5.370$ Å, and $c = 4.939$ Å). As shown in Table 2, progressive substitution of Co for Mn caused a substantial progressive decrease in the unit cell volume. This is due to the smaller ionic radius of Co$^{2+}$ (0.58 Å) compared with that of Mn$^{2+}$ (0.66 Å) with a coordination number of four. As the morphology and particle size of cathode materials affect their electrochemical performance, the morphology of the Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$ ($x = 0.25, 0.5,$ and $0.75$) compounds were calculated using Scherrer’s equation and the powder XRD patterns and were determined to be $42.8(3), 41.1(8), 41.0(7), 42.8(3)$ and $36.1(7)$ nm, respectively. These results indicate that the crystallite size of Li$_2$MnSiO$_4$ did not change with the substitution of Co for Mn.

![Figure 3. Le Bail refinement patterns of (a) Li$_2$MnSiO$_4$, (b) Li$_2$Mn$_{0.75}$Co$_{0.25}$SiO$_4$, (c) Li$_2$Mn$_{0.5}$Co$_{0.5}$SiO$_4$, (d) Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$, and (e) Li$_2$CoSiO$_4$.](image)

**Table 2.** Lattice parameters, crystallite sizes, and BET surface area of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$ ($x = 0.25, 0.5,$ and $0.75$), Li$_2$MnSiO$_4$, and Li$_2$CoSiO$_4$.

| Composition             | a (Å)      | b (Å)      | c (Å)      | V (Å$^3$) | Crystallite size (nm) | S$_{BET}$ (m$^2$ g$^{-1}$) |
|-------------------------|------------|------------|------------|-----------|-----------------------|-----------------------------|
| Li$_2$MnSiO$_4$         | 6.3185(2)  | 5.3832(3)  | 4.9736(2)  | 169.17(1) | 42.8(3)               | 43.0                        |
| Li$_2$Mn$_{0.75}$Co$_{0.25}$SiO$_4$ | 6.2970(9)  | 5.3958(1)  | 4.9687(8)  | 168.83(5) | 42.8(7)               | 43.0                        |
| Li$_2$Mn$_{0.5}$Co$_{0.5}$SiO$_4$ | 6.2856(1)  | 5.3932(9)  | 4.9587(7)  | 168.10(5) | 41.1(8)               | 44.0                        |
| Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$ | 6.2716(10) | 5.3831(9)  | 4.9381(1)  | 166.71(5) | 40.7(0)               | 43.7                        |
| Li$_2$CoSiO$_4$         | 6.2647(1)  | 5.3720(10) | 4.9245(1)  | 165.73(6) | 36.1(7)               | 42.7                        |
CoMn$_{0.5}$Co$_{0.5}$SiO$_4$ was confirmed via the EDS analysis. This indicates that Li$_2$Mn$_{0.5}$Co$_{0.5}$SiO$_4$ is a solid solution of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$ and Li$_2$CoSiO$_4$, which is in agreement with the powder XRD data.

**3.2 Electrochemical properties**

The electrochemical performance was investigated for Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75), Li$_2$MnSiO$_4$/C, and Li$_2$CoSiO$_4$/C cathode materials. Figure 6 shows the first and second galvanostatic charge–discharge curves for Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75), Li$_2$MnSiO$_4$/C, and Li$_2$CoSiO$_4$/C cycled at a current rate of 33 mA g$^{-1}$ over a voltage range of 1.5–4.5 V at 30°C. The first discharge capacities of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C and Li$_2$CoSiO$_4$/C were 171.2 and 148.7 mAh g$^{-1}$, respectively, and the corresponding coulombic efficiencies were 66.6% and 69.1%, respectively. During the first charge, Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75), Li$_2$MnSiO$_4$/C, and Li$_2$CoSiO$_4$/C exhibited voltage increases up to 4.3 V and a plateau (Fig. 6a–e). These data for Li$_2$MnSiO$_4$/C and Li$_2$CoSiO$_4$/C are consistent with the first charge curves previously reported by Aono et al. and Lyness et al., respectively. On the other hand, during the first and second discharges, Li$_2$CoSiO$_4$/C exhibited a well-defined plateau (Fig. 6e), while Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75) and Li$_2$MnSiO$_4$/C exhibited gradual voltage decreases to 1.5 V and no clear plateaus (Fig. 6a–d). These results for Li$_2$MnSiO$_4$/C and Li$_2$CoSiO$_4$/C are consistent with previous reports. In addition, the second charge curves for Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75) and Li$_2$MnSiO$_4$/C were different from the respective first charge curves (Fig. 6a–d).

To clarify the reason for these differences in the charge curves, XRD measurements of the uncharged, charged, and discharged cathodes were conducted. Figure 7 shows the XRD patterns of the uncharged, charged, and discharged cathodes of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75), Li$_2$MnSiO$_4$/C, and Li$_2$CoSiO$_4$/C. As can be seen in Fig. 7a–e, Al derived from current collector and typical diffraction lines of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75), Li$_2$MnSiO$_4$/C, and Li$_2$CoSiO$_4$/C were observed. However, peak intensities of these diffraction lines were lower than those of cathode materials (Fig. 2). This is due to the effect of cathode components such as current collector, binder, and conductive agent. In addition, the typical diffraction lines of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75) and Li$_2$MnSiO$_4$/C were not observed after the first charge to 4.5 V (Fig. 7a–d). This data for Li$_2$MnSiO$_4$/C is consistent with the XRD patterns previously reported by Do et al. and Li et al. In addition, these results indicate that the reason for the differences in the charge curves for the first and second cycles was the occurrence of irreversible structural changes during the first charge, as shown in Fig. 7a–d. On the other hand, the typical diffraction lines of Li$_2$CoSiO$_4$/C were very weak after the first charge to 4.5 V, which partially recovered after the first discharge (Fig. 7e). The different crystallinity of the first charge for Li$_2$CoSiO$_4$ compared with Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C (x = 0.25, 0.5, and 0.75) and Li$_2$MnSiO$_4$/C may be due to the difference degree of cation mixing.
between Co and Li. However, after the 10th discharge, the diffusion lines could not be distinguished from the background, indicating that irreversible structural changes occurred up to 10 charge–discharge cycles for the Li2CoSiO4 material. Notably, the electrochemical performance of Li2MnSiO4/C changed significantly with the substitution of Co for Mn. The first discharge capacities for Li2Mn0.75Co0.25SiO4/C, Li2Mn0.5Co0.5SiO4/C, and Li2Mn0.25Co0.75SiO4/C were 179.5, 186.2, and 202.5 mAh g−1, respectively, and Li2Mn0.25Co0.75SiO4/C exhibited the best electrochemical performance among all samples. These results indicate that the optimal Co substitution (75 mol%) for Mn in Li2MnSiO4/C enhances the material’s electrochemical performance. In addition, these results were compared to theoretical values, and the theoretical discharge capacities of Li2Mn1−xCoxSiO4 (x = 0, 0.25, 0.5, 0.75, and 1) calculated by Mn3+/4+, Mn3+/4+, and Co3+/4+ redox couples are shown in Fig. 8. As shown in this figure, the theoretical discharge capacities of the Co-substituted Li2MnSiO4/C decreased linearly with increasing Co content, as the Co3+/4+ redox couple could not be activated (the theoretical voltage is 5 V) over the voltage range of 1.5–4.5 V. The difference between the theoretical and practical discharge capacities decreased with increasing Co content. Li2Mn0.25Co0.75SiO4/C exhibited a discharge capacity (205 mAh g−1) close to the theoretical value. In addition, the first charge capacities of Li2Mn1−xCoxSiO4 (x = 0.5, and 0.75) and Li2CoSiO4 were higher than the theoretical ones. This high charge capacities are attributed to electrolyte decomposition.

To clarify the reason for the differences in the electrochemical performance of Li2Mn1−xCoxSiO4 (x = 0, 0.25, 0.5, 0.75, and 1), EIS measurements were performed on the cells at open circuit voltage for Li2Mn1−xCoxSiO4/C (x = 0.25, 0.5, and 0.75), Li2MnSiO4/C, and Li2CoSiO4/C, and the results are shown in Fig. 9. A semicircle at high frequencies and a straight line at low frequencies were observed for all samples, corresponding to the charge transfer resistance (RCT) and Warburg impedance due to Li+ diffusion inside the bulk of the cathode material, respectively. The calculated RCT values for Li2Mn1−xCoxSiO4/C (x = 0.25, 0.5, and 0.75), Li2MnSiO4/C, and Li2CoSiO4/C were 237, 224, 221, 206, and 176 Ω, respectively. These results indicate that RCT decreased as the Co content in Li2Mn1−xCoxSiO4/C increased. Therefore, the best discharge capacity of Li2Mn0.25Co0.75SiO4/C among Li2Mn1−xCoxSiO4 (x = 0, 0.25, 0.5, 0.75, and 1) was attributed to combined effect of the lower charge transfer resistance compared with that of Li2MnSiO4/C (Fig. 9) and the higher theoretical discharge capacity compared with that of Li2CoSiO4/C (Fig. 8).
Furthermore, the differential charge–discharge capacities \((dQ/dV)\) were calculated to observe the various changes in the reaction mechanism. Figure 10a–e shows the first and second \((dQ/dV)\) values plotted as a function of the voltage for \(\text{Li}_2\text{Mn}_1\text{Co}_x\text{SiO}_4/C\) \((x = 0.25, 0.5, \text{and } 0.75)\), \(\text{Li}_2\text{MnSiO}_4/C\), and \(\text{Li}_2\text{CoSiO}_4/C\); (i) uncharged; (ii) charged to 4.0 V in the first cycle; (iii) charged to 4.2 V in the first cycle; (iv) charged to 4.5 V in the first cycle; (v) discharged to 1.5 V in the first cycle; (vi) discharged to 1.5 V after 10 cycles at a current rate of 33 mA g\(^{-1}\) over a voltage range of 1.5–4.5 V at 30°C.

![Figure 7](image-url)

**Figure 7.** XRD patterns of the cathodes of (a) \(\text{Li}_2\text{MnSiO}_4\), (b) \(\text{Li}_2\text{Mn}_{0.75}\text{Co}_{0.25}\text{SiO}_4\), (c) \(\text{Li}_2\text{Mn}_{0.5}\text{Co}_{0.5}\text{SiO}_4\), (d) \(\text{Li}_2\text{Mn}_{0.25}\text{Co}_{0.75}\text{SiO}_4\), and (e) \(\text{Li}_2\text{CoSiO}_4\): (i) uncharged; (ii) charged to 4.0 V in the first cycle; (iii) charged to 4.2 V in the first cycle; (iv) charged to 4.5 V in the first cycle; (v) discharged to 1.5 V in the first cycle; (vi) discharged to 1.5 V after 10 cycles at a current rate of 33 mA g\(^{-1}\) over a voltage range of 1.5–4.5 V at 30°C.
Theoretical discharge capacity (mAh g\(^{-1}\)) vs. Co/(Mn+Co) (molar ratio)

Figure 8. Theoretical discharge capacities of Li\(_2\)Mn\(_{1-x}\)Co\(_x\)SiO\(_4\) (x = 0, 0.25, 0.5, 0.75, and 1) calculated by Mn\(^{2+/3+}\), Mn\(^{3+/4+}\), and Co\(^{2+/3+}\) redox couples over a voltage range of 1.5–4.5 V and the corresponding practical discharge capacities at a current rate of 33 mA g\(^{-1}\).

Electrochemical impedance plots of Li\(_2\)Mn\(_{1-x}\)Co\(_x\)SiO\(_4\) (x = 0.25, 0.5, and 0.75), Li\(_2\)MnSiO\(_4\), and Li\(_2\)CoSiO\(_4\). The inset shows the equivalent circuit used to analyze the data.

Figure 9. Electrochemical impedance plots of Li\(_2\)Mn\(_{1-x}\)Co\(_x\)SiO\(_4\) (x = 0.25, 0.5, and 0.75), Li\(_2\)MnSiO\(_4\), and Li\(_2\)CoSiO\(_4\). The inset shows the equivalent circuit used to analyze the data.

Figure 10. Differential capacities (dQ/dV) vs. voltage plots for (a) Li\(_2\)MnSiO\(_4\), (b) Li\(_2\)Mn\(_{0.75}\)Co\(_{0.25}\)SiO\(_4\), (c) Li\(_2\)Mn\(_{0.5}\)Co\(_{0.5}\)SiO\(_4\), (d) Li\(_2\)Mn\(_{0.25}\)Co\(_{0.75}\)SiO\(_4\), and (e) Li\(_2\)CoSiO\(_4\) at a current rate of 33 mA g\(^{-1}\) over a voltage range of 1.5–4.5 V at 30°C.
Co0.75SiO4, and Li2CoSiO4 at a current rate of 33 mA g⁻¹ (Fig. 10b) exhibited two distinguishable peaks at 3.3–4.5 V at 30°C as a function of the cycle number.

The cycling performances of Li2Mn1–xCoxSiO4 (x = 0.25, 0.5, and 0.75) (Fig.10b), Li2Mn0.25Co0.75SiO4, and Li2CoSiO4 at a current rate of 33 mA g⁻¹ over a voltage range of 1.5–4.5 V at 30°C as a function of the cycle number.

The cycling performances of Li2Mn1–xCoxSiO4 (x = 0.25, 0.5, and 0.75), Li2MnSiO4, and Li2CoSiO4 as a function of Co content. The cycling efficiencies of Li2Mn1–xCoxSiO4 (C, and Li2CoSiO4 as a function of Co content. The cycling efficiencies of Li2Mn1–xCoxSiO4 (x = 0.25, 0.5, and 0.75) were then tested at a current rate of 33 mA g⁻¹. From Fig. 11a–b, we can see that the capacity fades and the coulombic efficiencies observed for the samples were similar. Li2MnSiO4/C and Li2CoSiO4/C delivered discharge capacities of 171.1 and 148.7 mAh g⁻¹ for the first cycle, respectively, where their corresponding coulombic efficiencies were 66.6 and 69.1%, respectively. In subsequent cycles, the coulombic efficiency increased and then gradually decreased until the 20th cycle. However, at the 20th cycle, Li2MnSiO4/C delivered 49% and 51% of their first discharge capacities, respectively. This result is similar to the cycling performance of Li2MnSiO4/C previously reported by Liu et al.37 Capacity fading was also observed for Li2Mn1–xCoxSiO4/C (x = 0.25, 0.5, and 0.75); after 20 cycle, Li2Mn0.75Co0.25SiO4/C, Li2Mn0.5Co0.5SiO4/C, and Li2Mn0.25Co0.75SiO4/C delivered discharge capacities of 92.6, 98.3, and 90.3 mAh g⁻¹ and retained 52%, 53%, and 45% of the values of their first discharge capacities, respectively. This may be due to the instability of the crystal structure, as shown in Fig. 7b–d. The cycling efficiencies of Li2Mn1–xCoxSiO4/C (x = 0.25, 0.5, and 0.75) increased after a few cycles and gradually decreased until the 20th cycle. Further studies are needed to improve the cycling performance of Li2Mn1–xCoxSiO4/C.

Finally, rate capability studies were performed for Li2Mn1–xCoxSiO4/C (x = 0.25, 0.5, and 0.75), Li2MnSiO4/C, and Li2CoSiO4/C. Figure 12a–b shows the first discharge capacities and energy densities of Li2Mn1–xCoxSiO4/C (x = 0.25, 0.5, and 0.75), Li2MnSiO4/C, and Li2CoSiO4/C as a function of Co content. The discharge capacity and energy density of Li2MnSiO4/C (171.2 mAh g⁻¹ and 505.1 Wh kg⁻¹), respectively, at a current density of 33 mA g⁻¹ decreased linearly with increasing current density (110.0 mAh g⁻¹ and 285.0 Wh kg⁻¹, respectively, at a current density of 330 mA g⁻¹). On the contrary, the sensitivity of the

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**Figure 11.** (a) Discharge capacity and (b) coulombic efficiency of Li2MnSiO4, Li2Mn0.75Co0.25SiO4, Li2Mn0.5Co0.5SiO4, Li2Mn0.25Co0.75SiO4, and Li2CoSiO4 at a current rate of 33 mA g⁻¹ over a voltage range of 1.5–4.5 V at 30°C as a function of the cycle number.

**Figure 12.** (a) First discharge capacity and (b) energy density of Li2MnSiO4, Li2Mn0.75Co0.25SiO4, Li2Mn0.5Co0.5SiO4, Li2Mn0.25Co0.75SiO4, and Li2CoSiO4 at current rates of 33, 165, and 330 mA g⁻¹ over a voltage range of 1.5–4.5 V at 30°C as a function of Co/(Mn + Co) (molar ratio).
discharge capacity and energy density to the current density was substantially lower for Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C ($x = 0.25, 0.5$, and $0.75$) and Li$_2$CoSiO$_4$/C. The discharge capacity and energy density of Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$/C, which were the highest at a current density of 33 mA g$^{-1}$ ($202.5$ mAh g$^{-1}$ and $659.7$ Wh kg$^{-1}$, respectively), decreased to $163.6$ mAh g$^{-1}$ and $511.7$ Wh kg$^{-1}$, respectively, at a current density of $330$ mA g$^{-1}$ (19% reduction in discharge capacity). This indicates that energy density of Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$/C at a current density of $33$ mAh g$^{-1}$ was greater than that of conventional lithium transition metal oxides such as LiMn$_2$O$_4$ (500 Wh kg$^{-1}$) and LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (600 Wh kg$^{-1}$). Moreover, dependence of the discharge capacity in current density decreased as the Co content in Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C was observed. Although the capacity fades for Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C, the discharge capacity and rate capability of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C were similar to those of Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$/C. The synthesized Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C were attributed to its lower charge transfer resistance compared to that of Li$_2$MnSiO$_4$/C.

4. Conclusions

Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C ($x = 0.25, 0.5$, and $0.75$) materials comprising uniform nanosized primary particles and no impurities were successfully synthesized using a hydrothermal method, followed by carbon coating. Li$_2$MnSiO$_4$/C and Li$_2$CoSiO$_4$/C were also synthesized for comparison. The synthesized Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C ($x = 0.25, 0.5$, and $0.75$) materials were identified based on an orthorhombic unit cell with Pmn2$_1$ space group symmetry, and a solid solution was observed. Although the capacity fades for Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C ($x = 0.25, 0.5$, and $0.75$) was similar to those of Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$/C and Li$_2$CoSiO$_4$/C, the discharge capacity and rate capability of Li$_2$Mn$_{1-x}$Co$_x$SiO$_4$/C increased on substitution of Co for Mn, respectively. Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$/C exhibited the best electrochemical performance with first discharge capacities (and energy densities) as $202.5$mAh g$^{-1}$ (659.7 Wh kg$^{-1}$) and $163.6$mAh g$^{-1}$ (511.7 Wh kg$^{-1}$) at current rates of 33 and 330 mA g$^{-1}$, respectively. The good electrochemical performance of Li$_2$Mn$_{0.25}$Co$_{0.75}$SiO$_4$/C was attributed to its lower charge transfer resistance compared to that of Li$_2$MnSiO$_4$/C.

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