Research Article

Effect of 3D Metal on Electrochemical Properties of Sodium Intercalation Cathode P2-Na$_x$Me$_{1/3}$Mn$_{2/3}$O$_2$ (M = Co, Ni, or Fe)

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Received 25 July 2020; Revised 19 February 2021; Accepted 17 March 2021; Published 25 March 2021

Academic Editor: Mohamed Azaroual

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This research aims to evaluate the influence of different 3D metals (Fe, Co, and Ni) substituted to Mn on the electrochemical performance of P2-Na$_x$Me$_{1/3}$Mn$_{2/3}$O$_2$ material, which was synthesized by the coprecipitation process followed by calcination at high temperature. X-ray diffraction (XRD) results revealed that the synthesized Mn-rich materials possessed a P2-type structure with a negligible amount of oxide impurities. The materials possessed their typical cyclic voltammogram and charge-discharge profiles; indeed, a high reversible redox reaction was obtained by Na$_x$Co$_{1/3}$Mn$_{2/3}$O$_2$ sample. Both Na$_x$Co$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_x$Fe$_{1/3}$Mn$_{2/3}$O$_2$ provided a high specific capacity of above 140 mAh·g$^{-1}$; however, the former showed better cycling performance with 83% capacity retention after 50 cycles at C/10 and high rate capability. Meanwhile, the Ni-sub Na$_x$Ni$_{1/3}$Mn$_{2/3}$O$_2$ exhibited excellent cycling stability but a low specific capacity of 110 mAh·g$^{-1}$ and inferior rate capability. The diffusion coefficient of Na$^+$ ions into the structure tended to decrease with a depth of discharge; those values were in the range of 10$^{-10}$–10$^{-9}$ cm$^2$·s$^{-1}$ and 10$^{-11}$–10$^{-10}$ cm$^2$·s$^{-1}$ in the solid solution region and biphasic region, respectively.

1. Introduction

Lithium battery has been regarded as the best power source for mobile devices since it initially came to market. The energy demand for a lithium battery has been intensively increasing in recent years. With the unremitting efforts of several generations of scientists, the performance of lithium batteries has been greatly improved [1–3]. However, the development of lithium batteries is facing more and more serious challenges, such as resource scarcity, extraction difficulty, and high processing cost. To alleviate the lithium crisis, researchers have considered sodium to be a substitution for lithium. Compared to lithium, sodium possesses some superior features. The process of extraction of sodium from raw materials is not only cheaper, about a tenth of the cost of extraction of lithium, but also much technically simpler. It is noteworthy that sodium is the second lightest metallic element after lithium. Most importantly, the abundance of sodium on the earth is thousand times more than that of lithium. Lithium-ion batteries (LIBs) and
sodium-ion batteries (SIBs) have been studied since early 1970s. However, SIBs have been overshadowed by the development of LIBs for nearly two decades owing to the superior LIBs’ properties, such as high capacity, high power density, excellent cycle life, and the small-sized packing storage. In recent years, attention has been shifted to SIBs with the expectation of a prospective replacement for LIBs in large-scale applications [4]. The number of publications concerning SIBs has risen rapidly since 2010 and became comparable to that of LIBs [5].

Most studies of sodium battery are focusing on the development of electrodes of materials, especially cathode materials which is one of the decisive factors in the performance of a rechargeable battery. A diverse range of materials has been proposed as cathodes for SIBs. Polyanionic or phosphate-based compounds are easily recognized by their flat-voltage profile, high working potential, but relatively low capacity, while one has high capacity but low working voltage [6]. Therefore, layered 3D metal oxides (Na$_x$Me$_{1-x}$O$_2$) have attracted great attention in the field of cathode materials for SIBs, mainly because of their high capacity, highly reversible cycling ability, and the simplicity of synthesis [7, 8]. Among Na-intercalated cathode materials, P2-type Mn-based layered oxides have been considered one of the most promising candidates due to the low cost of synthesis [7, 8].

2.1. Material Synthesis. The Mn-rich materials were synthesized via the hydroxide coprecipitation method. The crystalline structure and electrochemical behaviors were investigated to evaluate the influence of different metal substitutions on their properties.

2.2. Material Characterization. X-ray diffraction (XRD) patterns of synthesized samples were recorded in 2θ range from 10° to 70° at ambient temperature in a D8 advanced (Bruker) diffractometer using CuK-$\alpha$ radiation ($\lambda = 1.5814\ \text{Å}$) at a scanning rate of 0.02° per step and 1 second per step. The lattice parameters of synthesized samples were obtained from Rietveld refinement using Material Studio 2017.

2.3. Electrochemical Investigation. A diverse range of materials has been proposed as cathodes for SIBs. Polyanionic or phosphate-based compounds are easily recognized by their flat-voltage profile, high working potential, but relatively low capacity, while one has high capacity but low working voltage [6]. Therefore, layered 3D metal oxides (Na$_x$Me$_{1-x}$O$_2$) have attracted great attention in the field of cathode materials for SIBs, mainly because of their high capacity, highly reversible cycling ability, and the simplicity of synthesis [7, 8]. Among Na-intercalated cathode materials, P2-type Mn-based layered oxides have been considered one of the most promising candidates due to the low cost of synthesis [7, 8]. Among Na-intercalated cathode materials, P2-type Mn-based layered oxides have been considered one of the most promising candidates due to the low cost of synthesis [7, 8]. Among Na-intercalated cathode materials, P2-type Mn-based layered oxides have been considered one of the most promising candidates due to the low cost of synthesis [7, 8]. Among Na-intercalated cathode materials, P2-type Mn-based layered oxides have been considered one of the most promising candidates due to the low cost of synthesis [7, 8].
3. Results and Discussion

3.1. Crystalline Structure and Morphology. Figure 1 shows the XRD patterns of as-prepared NaCMO, NaNMO, and NaFMO samples, which confirmed the crystallization of the materials in a hexagonal lattice with the space group P63/mmc (P21−Na0.58Ni1/3Mn2/3O2 as the standard, PDF#01-070-3726). Rietveld refinement of the materials was performed based on the structural model of the given standard. The low value of the χ² factor indicated that all patterns were well-fitted with the calculated models. The lattice parameters of the samples are listed in Table 1. The a and c parameters are almost the same for Co and Ni subsamples, while those of the Fe subsample are significantly larger. This resulted from the change in the Mn^{4+}/3+ ratio in the transition metal layers as well as the difference in ionic radii of substituting ions.

SEM images of the Mn-rich samples are shown in Figures 1(d)–1(f). The NaCMO exhibited flaky morphology with the particle size varying from 5 to 15 μm. The particles are agglomerated into larger secondary particles which have a polygonal shape and the size varying from 15 to 30 μm (Figure 1(d)). In contrast, NaNMO showed rod-like shape particles with the length varying in the range of 3–5 μm. Agglomeration was also observed, resulting in polygonal secondary particles with a diameter of 10–15 μm (Figure 1(e)). NaFMO had polygonal morphology, with the size of primary particles varying in the range of 2–4 μm (Figure 1(f)).

AAS results given in Table 2 confirmed that the ratio of Me:Mn in the samples was close to the expected ratios. A slight deviation from the ideal composition could be assigned to the difference in solubility of metal hydroxides in the synthesis step.

3.2. Electrochemical Behaviors. Cyclic voltammetry (CV) was applied to study the redox reactions and to determine the working voltage windows and electrochemical behaviors of the as-prepared Mn-rich samples (Figure 2). In general, the CV curves of the samples displayed similar features in the voltage range 1.5–4.8 V corresponding to redox reaction of Mn^{4+}/5+ and Me^{4+/2+}, respectively [13, 23]. As could be seen in the CV curves of the samples NaCMO and NaNMO (Figure 3), at least 4 peak couples characterized by the redox reactions of transition metals could be highlighted. In the case of NaCMO, the anode peaks were located at about 2.2 V, 2.9, 3.1 V, 3.6 V, and 4.4 V. For each of them, there was a corresponding cathode peak of similar intensity and position, proving the high reversibility of Co submaterial.

Different from NaCMO, peaks located at the high-voltage region of NaNMO showed quasi-reversibility. An anodic shifting of reduction peaks at the high-voltage region resulted in a merged peak at about 3.1 V. As could be noticed, peaks at the low-voltage region remained reversible. The quasi-reversible peak at 4.5 V is contributed from the P2–O2 phase transition due to slab gliding when Na⁺ content lowers as indicated by XRD in situ results elsewhere [24, 25].

The sample NaFMO also gave quasi-reversibility at the high-voltage region in the CV curve. The reduction peak shifted strangely to an anodic direction. The CV curve did not display anode peak at 3.7 V and 4.5 V, which were seen in CV curves of NaCMO and NaNMO. Besides, the reduction peak located at 3.2 V and 3.1 V exhibited unusual intensity compared to the intensity of anodic peak located at 4.1 V. This could be the result of reversible phase transition P2–OP4 at high potential and the slow reduction of the OP4 phase [26, 27]. Fe substitution could enhance the operational potential of the materials based on the high redox potential of Fe^{4+}/Fe^{3+} [27–29]. In the CV curve of NaFMO, the redox couple peaks shifted to a higher voltage direction compared to that of the other materials.

Since the anodic peaks above 4.1 V in the three CV curves were signals of irreversibility, the cycling performance of the Mn-rich samples was conducted in the voltage range of 1.5–4.1 V (vs. Na⁺/Na).

The first oxidations of the layered electrodes in sodium half-cell are shown in Figure 3. The open-circuit voltage (OCV) of NaCMO, NaNMO, and NaFMO were 2.50, 2.44, and 2.38 V, respectively. This agrees with the previous study [30], which reports the OCV of about 2.5 V vs. Na⁺/Na for P2-type layered structures. In the first charge, there were 0.24, 0.27, and 0.33 Na⁺ ion extracted from NaCMO, NaNMO, and NaFMO electrodes, respectively. Assuming that the initial Na⁺ content of the materials was 0.7, the number of Na⁺ ions retained in the oxidized cathodes was 0.46, 0.43, and 0.37 following the order above. The short plateau at 3.6 V in the first charge of NaCMO corresponded to the anodic peaks at high voltage in the CV curve (Figure 2(a)). The potential jump in the voltage region 3.3–3.5 V was similar to that in the charge curve of Co-contained electrodes [15, 23, 31]. Hence, it could be suggested that there were two phase transitions at 3.3 V and 3.5 V in a galvanostatic test of NaCMO. The voltage jump was also seen in the first charge curve of NaNMO. According to previous reports, the plateau at 3.7 V represented the oxidation of Ni^{3+} into Ni^{4+} and then Ni^{4+}. The potential jump in the first charge curve of NaFMO, to some extent, was less pronounced than the other counterparts. The plateaus at high and lower voltage correlated to the oxidation of Fe^{3+} to Fe^{4+} and Mn^{3+} to Mn^{4+}, respectively. However, the higher-voltage plateaus suppressed on the discharge curve could be the consequence of instability of Fe^{4+} ion and the migration of cation. Consequently, the redox reaction is irreversible, and the reduction reaction did not occur at a specific potential but kept until the iron cations are all reduced.

Figure 3 also exhibits the initial charge-discharge curves of three Mn-rich materials in the voltage range of 1.5–4.1 V (vs. Na⁺/Na). In the first cycle, NaCMO, NaNMO, and NaFMO allowed the intercalation of 0.58, 0.55, and 0.43 sodium ion on discharge, corresponding to the specific capacity of 147, 140, and 110 mAh·g⁻¹, respectively. Most of the capacities of NaCMO and NaNMO gained at the voltage region below 2.5 V might be due to the contribution of Mn^{4+}/Mn^{3+} redox reaction. The capacity of NaNMO, however, could partly arise from the contribution of Ni^{4+}/Ni^{3+}, while the Mn content was the same in the layered structures. The results indicated the greater contribution of
Figure 1: Rietveld refinement results for the as-prepared NaCMO sample (a), NaNMO sample (b), and NaFMO sample (c). SEM images of NaCMO sample (d), NaNMO sample (e), and NaFMO sample (f).

Table 1: Lattice parameters of the samples calculated from Rietveld refinement.

| Sample ID | $a$ (Å)  | $b$ (Å)  | $c$ (Å)  | $V$ ($Å^3$) |
|-----------|----------|----------|----------|-------------|
| NaCMO     | 2.8756   | 2.8756   | 11.2231  | 80.3712     |
| NaNMO     | 2.8808   | 2.8808   | 11.2097  | 80.5658     |
| NaFMO     | 2.9720   | 2.9720   | 11.3921  | 87.1429     |
Mn$^{4+}$/Mn$^{3+}$ couple to the specific capacity of NaCMO and NaFMO.

The stability of charge-discharge of the materials was investigated, and the results are shown in Figure 4. The symmetry between the charge and the discharge curves in a cycle exhibits a high reversible redox reaction of sodium intercalation/deintercalation. The charge-discharge profiles which are insignificant changed at the end of the cycle. Though, in the NaFMO sample, the overpotential of charge and discharge increased quite rapidly with cycle number, leading to the fast decrease of capacity after 50 cycles. Meanwhile, the NaCMO and NaNMO samples all remained relatively stable cycling so capacities fall slowly.

Figure 5 shows the capacity retention of three materials in sodium half-cell in a long-term cycling test. Comparing to pure P2-Na$_2$MnO$_2$, the doped-materials improved the capacity retention or cycle life, as indicated by various reports [20, 22, 32]. In this work, the specific capacity of NaCMO declined gradually, maintaining 82.87% of the initial capacity after 50 cycles. The coulombic efficiency was maintained at nearly 100% throughout the cycling. When Ni was introduced to the structure, the cycling performance of the material improved significantly. The initial specific capacity was 112 mAh·g$^{-1}$; 92% capacity retention after 50 cycles was obtained in NaNMO which was the highest capacity retention ability among three materials. In the first 20 cycles, the coulombic efficiency of NaNMO increased gradually from around 93% to 99% and then remained stable.

### Table 2: Chemical compositions of the samples determined by AAS.

| Sample ID | Mn   | Co/Ni/Fe | Empirical formula     |
|-----------|------|----------|-----------------------|
| NaCMO     | 36.4 | 17.9     | Na$_{x}$Co$_{0.315}$Mn$_{0.685}$O$_2$ |
| NaNMO     | 37.0 | 17.2     | Na$_{x}$Ni$_{0.303}$Mn$_{0.697}$O$_2$ |
| NaFMO     | 34.2 | 19.7     | Na$_{x}$Fe$_{0.361}$Mn$_{0.639}$O$_2$ |

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Figure 2: Cyclic voltammogram of the as-prepared samples in the voltage range of 1.5–4.8 V at 50 μV·s$^{-1}$. (a) NaCMO, (b) NaNMO, and (c) NaFMO.

Figure 3: The first galvanostatic charge-discharge of NaCMO, NaNMO, and NaFMO electrodes.
at this value up to the 50th cycle. NaFMO showed good
coulombic efficiency of nearly 100%, but poor cycling re-
tention (67.23% after 50 cycles). The reduction in capacity
could be attributed to the reversibility and inferior stability
of Fe^{3+}/Fe^{2+} redox couple at high voltage. The problem also
happens in several cathodes that combined Mn and Fe,
suggesting that the use of the elements which are all unstable
did not improve the performance stability of manganese
cathode. On the other hand, it could be deduced that the Co
substitution, which is high conductivity and high voltage
stable, provided high specific capacity and improved long-
term workability of the Mn-based layered structure.
Meanwhile, the Ni-Mn system exhibited superior cycling
stability but lower capacity. Therefore, Co-Mn gave the best
performance over the other two Mn-based systems.

Figure 6 demonstrates the rate capability performances
of three Mn-rich materials. In the cases of NaCMO and
NaNMO, the cycling performances were quite stable re-
gardless of the current density and the capacity recovered to
the initial value without any loss when the current density
was switched back to C/10. Noticeably, NaCMO exhibited
superior high-rate performance. At the current density of
C/5, the specific capacity retained 87% (123 mAh·g^{-1}) of that
at current density C/10. When the current density increases
from C/5 to 2C, the specific capacity slightly decreased from
123 mAh·g^{-1} (C/5), 109 mAh·g^{-1} (C/2), and 99 mAh·g^{-1}
(1C) to 88 mAh·g^{-1} (2C) (77%, 70%, and 62% of initial
capacity, respectively). The high rate capability was due to
the enhanced effect of cobalt on the material ionic and
electronic conductivity.

Contrary to the excellent performance of NaCMO,
NaNMO was not suitable for working at a high current rate.
A significant capacity decreased to 100%, 76%, and 42% of
initial capacity when the current density increased from
122 mAh·g^{-1} (C/10), 93 mAh·g^{-1} (C/5), and 51 mAh·g^{-1}
at C/2, respectively. At the current density of 1C, about 87%
of the initial capacity of NaNMO was lost. Compared to Ni sub
and Co subcounterparts, NaFMO showed poor performance
not only at a high current rate but also in capacity recovery.
At the current density of C/5 and C/2, NaFMO was able to
maintain 75% (109 mAh·g^{-1}) and 42% (61 mAh·g^{-1}) of its
initial capacity (145 mAh·g^{-1}), respectively, which are much
lower than the other two systems.

The kinetics of Na^{+} ions diffusion into the Mn-rich
electrodes during the Na-insertion was investigated through
diffusion coefficient determined by GITT technique. The cell
was initially applied a constant charge current to 4.1 V and then discharged at a constant current density of C/100 for a time interval of 1 hour followed by a relaxation period of 6 hours, which allows the cell to reach equilibrium voltage ($E_s$). The diffusion coefficients were calculated from the following equation:

$$D_{Na} = \frac{4I_o V_m}{\pi F S} \left( \frac{dE}{dx} \right)^2, \quad (1)$$

where $I_o$ is the discharge current (A); $V_m$ is the molar volume of the electrode (cm$^3$·mol$^{-1}$); $F$ is the Faraday constant (96485 C/mol); $S$ is the electrode/electrolyte contact area (cm$^2$); $dE/dx$ is the slope of the coulometric titration curve, determined by plotting the $E_s$ (V) measured after each titration step versus $x$; and $dE/dt^{1/2}$ is the slope of the linearized plot of the potential $E$ (V) versus $t^{1/2}$ ($t$ is measured in second).

Figure 7 illustrates the evolution of Na$^+$ ions diffusion coefficients calculated in the first discharge of NaCMO, NaNMO, and NaFMO. The evolution of structure during Na$^+$ ions intercalation could be divided into regions that appeared in the voltage profile as a flat-voltage region (around 1.5–2 V), sloping region (around 2–3.2 V), and stepping region (the rest). Generally, $D_{Na}$ gradually decreased during Na$^+$ ion intercalation due to reduction of diffusion length with many sudden decrease or increase due to diffusion through the boundary between phases in the phase transfer region [33, 34]. Due to the complexity of phase transition of NaNMO during sodiation, appearance as many short-voltage plateaus in the charge-discharge curves results in many fluctuations of $D_{Na}$. In the stepping region,
the $D_{Na}$ values were obtained around $10^{-9}$ cm$^2$s$^{-1}$. The $D_{Na}$ values decreased gradually in the transition sloping region to about $10^{-11}$-$10^{-10}$ cm$^2$s$^{-1}$ in the flat-voltage region at the end of discharge.

The evolution of the $D_{Na}$ value with the intercalation state during discharge is quite similar in the three samples but different in the magnitude of the $D_{Na}$ value. NaFMO displayed the best appearance of the $D_{Na}$ value but the worst performance in sodium half-cell. On the other hand, the stability of Na$^+$ ion diffusion in NaCMO is in agreement with the best performance in the three samples.

4. Conclusion

In summary, different substituting metals (Fe, Co, and Ni) have different effects on the performance of P2-Na$_x$Me$_{1/3}$Mn$_{2/3}$O$_2$ in Na-ion batteries. NaFMO provided the highest specific capacity (147 mAh g$^{-1}$) but poor cycling retention and poor rate capability. In contrast, NaCMO cathodes exhibited an initial specific capacity of 140 mAh g$^{-1}$ and better stamina at high current rates (1C and 2C). NaNMO showed superior cycling retention up to the 50$^{th}$ cycle. These electrochemical results indicated the roles of 3D metals in layered materials; Mn and Co stabilized the framework and increased electronic conductivity that resulted in high rate capability, while Ni helped to retain capacity, which is essential for long-term utilization.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The research work was supported by the National Foundation for Science and Technology Development (NAFOSTED) through the research project (104.06-2018.359).

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