Research Article

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

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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 $\text{P2-Na}_x\text{Me}_{1/3}\text{Mn}_{2/3}\text{O}_2$ 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 $\text{Na}_x\text{Co}_{1/3}\text{Mn}_{2/3}\text{O}_2$ sample. Both $\text{Na}_x\text{Co}_{1/3}\text{Mn}_{2/3}\text{O}_2$ and $\text{Na}_x\text{Fe}_{1/3}\text{Mn}_{2/3}\text{O}_2$ provided a high specific capacity of above $140 \text{ mAh}\cdot\text{g}^{-1}$; 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 $\text{Na}_x\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ exhibited excellent cycling stability but a low specific capacity of $110 \text{ mAh}\cdot\text{g}^{-1}$ 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} – $10^{-9} \text{ cm}^2\cdot\text{s}^{-1}$ and 10^{-11} – $10^{-10} \text{ cm}^2\cdot\text{s}^{-1}$ 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. Poly-anionic 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_xMeO_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 and abundance of raw materials [9, 10]. Previous studies on P2- $\text{Na}_{2/3}\text{MnO}_2$ showed a large specific capacity of $190 \text{ mAh}\cdot\text{g}^{-1}$ with good cycling retention [10–12]. Despite the advantages, P2- $\text{Na}_{2/3}\text{MnO}_2$ suffers from lattice distortion from hexagonal to orthorhombic induced by cooperative Jahn–Teller distortion (JTD) of six-coordinate Mn^{3+} ($t_{2g}^3 - e_g^1$). During the charge-discharge process, the redox couple $\text{Mn}^{4+}/\text{Mn}^{3+}$ is considered the main cause of large and anisotropic volume change, so Mn^{3+} ion has been regarded as an inadequate component that should be eliminated from battery materials. As a sequence, a recent strategy based on the idea of maintaining the average oxidation state of manganese close to +4 to avoid the Jahn–Teller effect of Mn^{3+} by different metallic substitution has been carried out. Mn-rich P2- $\text{Na}_{2/3}\text{Me}_x\text{Mn}_{1-x}\text{O}_2$ ($0.1 \leq x \leq 0.5$) materials, in which M can be either Co, Ni, or Fe, has been widely studied in recent years due to the aforementioned merits [9, 13–22].

In this work, $\text{Na}_x\text{Me}_{1/3}\text{Mn}_{2/3}\text{O}_2$ (Me = Co, Ni, and Fe) materials were synthesized via the hydroxide coprecipitation method. Their crystalline structure and electrochemical behaviors were investigated to evaluate the influence of different metal substitutions on their properties.

2. Experimental

2.1. Material Synthesis. The Mn-rich materials were synthesized via the hydroxide coprecipitation method. 10 mL of 3 M solution was prepared by dissolving $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ and metal salts, either $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, or $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, at the molar ratio 2 : 1 (solution A) and heated to 50°C . Separately, 25 mL of NaOH 4 M (solution B) was heated at 50°C and stirred inside a three-necked round flask under an N_2 inert atmosphere. Solution A was dripped into the flask

containing solution B in about 5 minutes. The mixture was kept at 50°C and stirred at 500 rpm for 15 hours. The slurry obtained in the bottom of the flask was then filtered, washed many times by distilled water until reaching neutral pH, and then dried at 50°C under vacuum for 15 hours.

The hydroxide precursors $\text{Me}_{1/3}\text{Mn}_{2/3}(\text{OH})_2$ and Na_2CO_3 were mixed at the molar ratio $\text{Na} : (\text{Me} + \text{Mn}) = 0.7 : 1.0$ and were treated under a three-step heat treatment: decomposition at 500°C for 6 hours, followed by calcination at 1000°C for 36 hours and annealing at 850°C for 6 hours. Then, the samples were transferred to an argon-filled glove box for cooling. The obtained samples were marked as NaCMO, NaNMO, and NaFMO, which were $\text{Na}_{2/3}\text{Co}_{1/3}\text{Mn}_{2/3}\text{O}_2$, $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$, and $\text{Na}_{2/3}\text{Fe}_{1/3}\text{Mn}_{2/3}\text{O}_2$, respectively.

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 $\text{CuK}\alpha$ radiation ($\lambda = 1.5814 \text{ \AA}$) at a scanning rate of 0.02° per step and 1 second per step. The phase component and crystalline structure were determined by comparing with standard XRD patterns using X'Pert HighScore Plus software. The lattice parameters were obtained from Rietveld refinement using Material Studio 2017.

The morphology of these samples was examined using a Hitachi FE-SEM S-4800 scanning electron microscope (SEM) with an accelerating voltage of 10 kV. The ratio of Mn and doping elements was determined by atomic absorption spectroscopy (AAS) on Shimadzu AA-6650F.

2.3. Electrochemical Investigation. The preparation of electrode and cell assembly was handled in an argon-filled glove box. The positive electrode consisted of Mn-rich material (80%), carbon (Super C65) (15%), and solid polytetrafluoroethylene (PTFE) (5%). The mixture was ground, rolled, and pressed into a thin film and cut into round-shaped pieces of 10 mm diameters. The cathode films were dried at 50°C using a hot plate before assembled in Swagelok-type sodium half-cell using a sodium slice as an anode, 3 glass filters (Whatman) as a separator, and the solution of 1 M NaClO_4 in PC-FEC (98 : 2) as the electrolyte.

Electrochemical characterization of half-cells was performed on galvanopotentiostat MPG2 (BioLogic) controlled by EC-Lab software (version 10.36). Cyclic voltammetry was scanned in the voltage range of 1.5–4.8 V (vs. Na^+/Na) at $50 \mu\text{V}\cdot\text{s}^{-1}$. Cycling performances were examined at standard C/10 rate and various current rates from C/10 to 2C in the potential range of 1.5–4.1 V to investigate rate capability (1C rate is the current to insert/extract one sodium in 1 hour corresponding to $\sim 240 \text{ mA/g}$). Kinetics of Na migration were evaluated through diffusion coefficients of Na^+ ions using the galvanostatic intermittence titration technique (GITT). The cells were discharged from 4.1 V at rate C/100 for 1 hour (corresponding to the insertion of 0.01 Na^+ per step) followed by relaxation for 6 hours. The GITT cycles were continued until the voltage reached 1.5 V.

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 $P6_3/mmc$ ($P2\text{-Na}_{0.58}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ 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 χ^2 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 $\text{Mn}^{4+/3+}$ 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 $\text{Mn}^{4+/3+}$ and $\text{Me}^{4+/2+}$, 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 quasireversibility. 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 quasireversible 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 quasireversibility 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 $\text{Fe}^{4+}/\text{Fe}^{3+}$ [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^{2+} into Ni^{3+} 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 $\text{mAh}\cdot\text{g}^{-1}$, respectively. Most of the capacities of NaCMO and NaFMO gained at the voltage region below 2.5 V might be due to the contribution of $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox reaction. The capacity of NaNMO, however, could partly arise from the contribution of $\text{Ni}^{4+}/\text{Ni}^{2+}$, 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	Lattice parameters			
	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	V ($\text{\AA}^3$)
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

TABLE 2: Chemical compositions of the samples determined by AAS.

Sample ID	Element percentage (%)		Empirical formula
	Mn	Co/Ni/Fe	
NaCMO	36.4	17.9	$\text{Na}_x\text{Co}_{0.315}\text{Mn}_{0.685}\text{O}_2$
NaNMO	37.0	17.2	$\text{Na}_x\text{Ni}_{0.303}\text{Mn}_{0.697}\text{O}_2$
NaFMO	34.2	19.7	$\text{Na}_x\text{Fe}_{0.361}\text{Mn}_{0.639}\text{O}_2$

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

FIGURE 3: The first galvanostatic charge-discharge of NaCMO, NaNMO, and NaFMO electrodes.

$\text{Mn}^{4+}/\text{Mn}^{3+}$ 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 $\text{P2-Na}_{2/3}\text{MnO}_2$, 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 $112 \text{ mAh}\cdot\text{g}^{-1}$; 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

FIGURE 4: The galvanostatic cycle of NaCMO (a), NaNMO (b), and NaFMO (c) in sodium half-cell.

FIGURE 5: Cycling retention and coulombic efficiency of NaCMO, NaNMO, and NaFMO in 50 cycles in sodium half-cell.

at this value up to the 50th cycle. NaFMO showed good coulombic efficiency of nearly 100%, but poor cycling retention (67.23% after 50 cycles). The reduction in capacity could be attributed to the irreversibility and inferior stability of $\text{Fe}^{4+}/\text{Fe}^{3+}$ 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 regardless 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% ($123 \text{ mAh}\cdot\text{g}^{-1}$) of that at current density C/10. When the current density increases from C/5 to 2C, the specific capacity slightly decreased from $123 \text{ mAh}\cdot\text{g}^{-1}$ (C/5), $109 \text{ mAh}\cdot\text{g}^{-1}$ (C/2), and $99 \text{ mAh}\cdot\text{g}^{-1}$ (1C) to $88 \text{ mAh}\cdot\text{g}^{-1}$ (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 $122 \text{ mAh}\cdot\text{g}^{-1}$ (C/10), $93 \text{ mAh}\cdot\text{g}^{-1}$ (C/5), and $51 \text{ mAh}\cdot\text{g}^{-1}$ 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% ($109 \text{ mAh}\cdot\text{g}^{-1}$) and 42% ($61 \text{ mAh}\cdot\text{g}^{-1}$) of its initial capacity ($145 \text{ mAh}\cdot\text{g}^{-1}$), 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

FIGURE 6: Rate capability performances of NaCMO, NaNMO, and NaFMO electrodes.

FIGURE 7: Evolution of sodium diffusion coefficient D_{Na} into NaCMO (a), NaNMO (b), and NaFMO (c) hosts in the first discharge.

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:

$$D_{\text{Na}} = \frac{4}{\pi} \left(I_0 \frac{V_m}{FS} \right)^2 \left(\frac{dE/dx}{dE/dt^{1/2}} \right)^2, \quad (1)$$

where I_0 is the discharge current (A); V_m is the molar volume of the electrode ($\text{cm}^3 \cdot \text{mol}^{-1}$); 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 $10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$. The D_{Na} values decreased gradually in the transition sloping region to about 10^{-11} – $10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ 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 $\text{P2-Na}_x\text{Me}_{1/3}\text{Mn}_{2/3}\text{O}_2$ in Na-ion batteries. NaFMO provided the highest specific capacity ($147 \text{ mAh} \cdot \text{g}^{-1}$) but poor cycling retention and poor rate capability. In contrast, NaCMO cathodes exhibited an initial specific capacity of $140 \text{ mAh} \cdot \text{g}^{-1}$ and better stamina at high current rates (1C and 2C). NaNMO showed superior cycling retention up to the 50th 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.

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