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MOF-Derived Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC Composite Anode Materials towards High-Performance Na-Ion Storage

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Abstract: Binary transition metal selenides (BTMSs) are more promising than single transition metal selenides (TMS) as anode materials of sodium-ion batteries (SIBs). However, it is still very challenging to prepare high-performance BTMSs in the pure phase, instead of a mixture of two TMSs. In this study, a binary metal center-based MOF derived selenization strategy was developed to prepare iron–cobalt selenide (Fe$_2$CoSe$_4$@NC) and iron–nickel selenide (Fe$_2$NiSe$_4$@NC) nanocomposites in the single phase and when wrapped with carbon layers. As the anode material of SIBs, Fe$_2$CoSe$_4$@NC exhibits higher long-term cycling performance than Fe$_2$NiSe$_4$@NC, maintaining a capacity of 352 mAh g$^{-1}$ after 2100 cycles at 1.0 A g$^{-1}$, which is ascribed to the higher percentage of the nanopores, larger lattice spacing, and faster Na$^+$ diffusion rate in the electrode materials of the former rather than the latter.

Keywords: bi-metal selenide; MOF; selenization; robust structure; diffusion

1. Introduction

As a promising candidate for energy storage systems, sodium-ion batteries (SIBs) have garnered significant attention owing to the low cost and wide availability of sodium [1–7]. However, the larger radius of sodium ions (1.02 Å) than lithium ions (0.76 Å) leads to a slow kinetic of sodium ion insertion and extraction [8–12]. The commonly used cathode materials for LIBs are Na$_3$V$_2$(PO$_4$)$_3$ and Prussian blue (PB), etc., with large open frames [13,14], while there more options for anode materials of LIBs [15–17]. The pursuit of optimal cathode and anode materials towards the achievement of SIBs with prolonged cycle life and substantial specific capacity presents a significant and formidable challenge for researchers [18,19].

In recent years, transition metal selenides (TMSs) have garnered extensive attention as anode materials for sodium-ion batteries (SIBs), owing to their high theoretical capacity [20,21]. For example, our group has developed ZIF-67-derived CoSe$_2$ nanoparticles (CoSe$_2$@NCF/CNTs) wrapped with N-doped and CNT-entangled carbonaceous materials [8]. The overall structural morphology of CoSe$_2$@N-CF/CNTs composites is well preserved, as anode materials of SIBs, even after 100 cycles at a current density of 1 A g$^{-1}$, demonstrate the effectiveness of carbonaceous material encapsulation in maintaining structural integrity. However, the electrochemical properties of TMSs anodes are constrained by challenges such as volume expansion and dissolution of polyselenide during cycling, leading to reduced conductivity and inferior electrochemical performance [17,22–24].

Binary transition metal chalcogenides (BTMCs), due to their improved electrochemical performance compared to single-metal compounds, have garnered significant attention.
The improved performance of binary transition metal selenides (BTMS) as the anode materials of SIBs is ascribed to their superior conductivity, endowed by the smart choice of metal elements in combination, and coupled, with the engineering of nanostructures [8,25,26]. For instance, hierarchically porous nanospheres of binary iron-cobalt selenide (Fe₂CoSe₄) were prepared using a hydrothermal method to obtain Fe-Co glycerate and further selenization using Se powder as a selenium precursor in hydrogen gas atmosphere, which exhibits an impressive rate capability and extended life cycle [8]. In another study, three types of binary transition metal selenides based on nickel–cobalt, nickel–iron, and cobalt–iron combinations were prepared with nanosheet structures, and nickel–iron selenide exhibits the longest cycling performance and highest charge capacity [25]. However, exploration towards the synthesis of BTMS and their application as anode materials SIBs are still very limited, since it is still very challenging to prepare a binary transition metal selenide (M₁,M₂,Seₓ₂, M₁, and M₂ are two different transition metal atoms) in the single phase, instead of mixed two types of metal selenides (M₁,Seₓ/M₂,Seₓ) [27]. Additionally, the mechanism behind the difference in the electrochemical performance of different combinations of these transition metal selenides remains unexplored.

Herein, we study MOF-derived bimetallic selenides, namely, iron–cobalt selenide (Fe₂CoSe₄@NC) and nickel–iron selenide (Fe₂NiSe₄@NC). Both Fe₂CoSe₄@NC and Fe₂NiSe₄@NC exhibited outstanding long-term cycling stability and rate capability, maintaining a capacity of 352 and 282.2 mAh g⁻¹ after 2100 cycles at 1.0 A g⁻¹, respectively. Both the electrolyte’s penetration of the porous electrode surface and the sodium ion conductance in the anode materials might govern the electrochemical performance of sodium-ion storage.

2. Results

Fe₂CoSe₄@NC and Fe₂NiSe₄@NC were synthesized with the selenization of a binary transition metal organic framework (MOF). Initially, a mixture of FeCo-MOF or FeNi-MOF and selenium powder was maintained at 300 °C for 4 h to ensure the complete selenization of the metal ligands. Subsequently, the sample was further annealed at 700 °C to fully carbonize the MOF structure to obtain carbon-wrapped BTMS. The crystal structure of the Fe₂CoSe₄@NC and Fe₂NiSe₄@NC samples was initially examined using XRD, as depicted in Figure 1a,b. The diffraction pattern in Figure 1a,b exhibits several peaks that can be accurately indexed to Fe₂CoSe₄@NC (JCPDS 89-1967) and Fe₂NiSe₄@NC (JCPDS 89-1968) without any detectable impurities [8]. This confirms the efficacy of our proposed strategy for the facile synthesis of BTMS in the pure phase. Fe₂CoSe₄@NC and Fe₂NiSe₄@NC show very similar diffraction patterns. The four diffraction peaks, with a high intensity identified at 32.9° to 33.9°, were ascribed to the reflection of (−2 0 2), (−1 1 2), (1 1 2), and (2 0 2), and the two prominent peaks at 44° and 44.7° were indexed to (−1 1 4) and (1 1 4). Another two evident peaks were identified at 51.49° and 51.59°, which were from the (310) and (0 2 0) planes. Although the diffraction positions of these prominent peaks are quite similar to each other, for Fe₂CoSe₄@NC and Fe₂NiSe₄@NC, the relative peak intensities were different from one another. For instance, the peak intensity of (−1 1 2) is slightly higher than that of (1 1 2) for Fe₂CoSe₄@NC, but it is the opposite case for Fe₂NiSe₄@NC, indicating the orientation difference of the lattice reflections of Fe₂CoSe₄@NC and Fe₂NiSe₄@NC. Additionally, the diffraction peak position of (−1 1 4) and (1 1 4) of Fe₂CoSe₄@NC negatively shifted compared to the standard peak, due to the lattice extension of (−1 1 4) and (1 1 4) planes, while no apparent shift was observed for Fe₂NiSe₄@NC. It should also be noted that the peaks of (310) and (0 2 0) planes are well resolved for Fe₂CoSe₄@NC, but emerged as one peak for Fe₂NiSe₄@NC, indicating the higher crystallinity of Fe₂CoSe₄@NC compared to Fe₂NiSe₄@NC.

The N₂ adsorption/desorption isotherms of Fe₂CoSe₄@NC and Fe₂NiSe₄@NC (Figure 1c) exhibit a type IV isotherm with a hysteresis loop at a relatively high pressure, indicating their mesoporous characteristics [11]. Both Fe₂CoSe₄@NC (75.02 m² g⁻¹) and Fe₂NiSe₄@NC (80.66 m² g⁻¹) display similar specific surface areas. The pore-size dis-
tribution of the Fe$_2$CoSe$_4$@NC sample, calculated using the Barrett–Joyner–Halenda (BJH) method, ranges from 3.8 to 14.4 nm (Figure 1d), including a narrow distribution at 4.8 nm and a broad distribution at around 7.5 nm, with a much higher percentage for the smaller pores than the larger ones. On the other hand, the pore size distribution of the Fe$_2$NiSe$_4$@NC sample was predominantly centered around 4.3–10 nm, with the maximum peak intensity being 7.3 nm. This indicates that the pore size in Fe$_2$CoSe$_4$@NC is relatively smaller than that of Fe$_2$NiSe$_4$@NC. It has been reported that the mesoporous nature and large surface area of electrode materials can enhance the electrolyte penetration, surface contact with electrolyte, and the interaction with sodium-ions, as well as increasing electronic conductivity by reducing the ion diffusion length [8].

The morphology of the nanocomposites was examined using scanning electron microscopy (SEM), as depicted in Figure 2a,b. In Figure 2a, SEM images of Fe$_2$CoSe$_4$@NC reveal random nanoparticles and nano-blocks, along with small pores on the surface. On the other hand, the SEM image of Fe$_2$NiSe$_4$@NC displays a noticeable agglomeration of nanoparticles (Figure 2b). The high-resolution transition electron microscopy (HRTEM) image of Fe$_2$CoSe$_4$@NC (Figure 2c) shows the calculated lattice spacing of 2.66 Å for (202) plane, which is slightly larger than that of Fe$_2$NiSe$_4$@NC (2.62 Å) (Figure 2d), consistent with the results obtained from the XRD patterns [25].

The carbon content in the Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC composites was evaluated using TGA, as shown in Figure S1. The percentages of TGA products for Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC were measured as 44.68% and 41.44%, respectively. According to the XRD (Figure S2), the TGA products of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC were identified to be (CoFe$_2$)O$_4$ and (NiFe$_2$)O$_4$, respectively. Based on the stoichiometry of the chemical reaction Fe$_2$CoSe$_4$@NC (s) + 3 O$_2$ (g) = (CoFe$_2$)O$_4$ (s) + 4 SeO$_2$ (g), the content of Fe$_2$CoSe$_4$ is calculated to be approximately 92.6 wt%, suggesting a carbon content of about 7.3 wt%. Similarly, the carbon content of Fe$_2$NiSe$_4$@NC is calculated to be about 14.0 wt%.

Figure 1. XRD patterns of (a) Fe$_2$CoSe$_4$@NC and (b) Fe$_2$NiSe$_4$@NC. (c) N$_2$ adsorption/desorption isotherms and (d) the corresponding Barret–Joyner–Halenda (BJH) pore size distribution of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC.
The chemical composition and valence states of elements in Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC composites were analyzed using X-ray Photoelectron Spectroscopy (XPS). Figure S3 presents the full survey spectra of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC, revealing the presence of Fe, Co, Se, C, O, and N elements in Fe$_2$CoSe$_4$@NC, and Fe, Ni, Se, C, O, and N elements in Fe$_2$NiSe$_4$@NC, respectively. The high-resolution Fe 2p spectra of Fe$_2$CoSe$_4$@NC (Figure 3a) and Fe$_2$NiSe$_4$@NC (Figure 3d) exhibit two peaks at 710.9 and 724.5 eV, corresponding to the Fe$^{2+}$ 2p$_{3/2}$ and 2p$_{1/2}$ orbitals [28], respectively, with two satellite peaks (marked with “Sat.”) [29,30]. The Co 2p of Fe$_2$CoSe$_4$@NC (Figure 3b) exhibits peaks at 780.3 and 796.3 eV, which are attributed to the Co$^{2+}$ 2p$_{3/2}$ and 2p$_{1/2}$ orbitals, accompanied with two satellite peaks at 785.9 and 802.8 eV, respectively [31–35]. As depicted in Figure 3e, the high-resolution XPS spectrum of Ni$^{2+}$ 2p comprises a pair of spin-orbit doublets at 854.6 and 873.2 eV, as well as two satellite peaks [36,37].

The spectra of Se 3d (Figure 3c,f) for Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC are well fitted, with two peaks corresponding to Se 3d$_{3/2}$ and 3d$_{5/2}$. The two peaks at 54.6 eV and 55.9 eV corresponds to Se 3d$_{3/2}$ and Se 3d$_{5/2}$, respectively. An additional peak located at 58.8 eV may be attributed to SeO$_x$ species [38], consistent with previous reports. The XPS analysis above evidently indicate that the Fe$_2$CoSe$_4$@NC sample contains Fe$^{2+}$, Co$^{2+}$, and Se$^{2−}$, while Fe$_2$NiSe$_4$@NC comprises species of Fe$^{2+}$, Ni$^{2+}$, and Se$^{2−}$, consistent with the literature [39–41].

The Raman bands at 1350 and 1576 cm$^{-1}$ are indexed to amorphous carbon (D band) and graphitic carbon (G band) [42]. The I$_D$/I$_G$ values for Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC were 0.97 and 0.94, respectively (Figure S4), indicating higher graphitization of Fe$_2$CoSe$_4$@NC than Fe$_2$NiSe$_4$@NC [43].

The storage properties of the sodium-ion of the Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC anodes were assessed through cyclic voltammetry (CV) in a half-cell configuration, wherein CR2032-type cells were assembled with Na foil serving as a counter electrode. Figure 4a illustrates the first CV cycle of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC as an anode of SIBs within the voltage range of 0.5–3.0 V, which was conducted at a scan rate of 0.2 mV s$^{-1}$. The significant peak near 1.10 V in the cathodic scans for the Fe$_2$CoSe$_4$@NC electrode, which
was not observed in the subsequent scan, and can be mainly attributed to electrolyte decomposition and the formation of a solid electrolyte interphase (SEI), as well as the conversion of Fe$_2$CoSe$_4$@NC to Na$_2$Se and Na$_x$Fe$_2$CoSe$_{4-x}$, as described in Equations (1)–(3) [35,44].

Figure 3. High-resolution XPS spectra of (a) Fe 2p, (b) Co 2p, and (c) Se 3d for Fe$_2$CoSe$_4$@NC, and (d) Fe 2p, (e) Co 2p, and (f) Se 3d for Fe$_2$NiSe$_4$@NC.

Figure 4. Na-storage properties of the Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC electrodes as anodes: (a) the first and (b) second cycle of CV curves for Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC at 0.2 mV s$^{-1}$ within 0.5–3.0 V; (c) the first three cycles of the CV curves for Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC; and (d) the EIS spectra of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC electrodes before and after cycling at 0.1 A g$^{-1}$.
In the second cycle of the CV scan, Fe₈CoSe₄@NC (Figure 4b) exhibits three cathodic peaks at 1.84, 1.24, and 0.75 eV, respectively, corresponding to sodiation reactions [8]. It should be noticed that the cathodic peak intensity at 1.10 V in the first scan was much decreased in the second scan, due to the stable formation SEI film in the first scan. In the second cycle of Fe₈NiSe₄@NC (Figure 4b), four distinct cathodic peaks are observed at 1.70, 1.43, 1.01, and 0.77 eV, respectively, corresponding to the naturalization reactions (4)–(7), respectively [28,45]. The cathodic peak at 0.77 eV remains very intense, indicating more complicated reactions involved in the discharging process of the Fe₈NiSe₄@NC electrode than the Fe₈CoSe₄@NC electrode. The second and third CV scans (Figure 4c) overlap very well with each other for both the Fe₈CoSe₄@NC and Fe₈NiSe₄@NC electrodes, suggesting a reversible and stable cycling performance.

To further investigate the interfacial charge transfer kinetics of the Fe₈CoSe₄@NC and Fe₈NiSe₄@NC electrodes, electrochemical impedance spectroscopy (EIS) was conducted within a frequency range of 0.1 Hz to 100 kHz. As depicted in Figure 4d, the Nyquist plots of both fresh electrodes exhibit a semicircle in the high-frequency region and a slanted line in the low-frequency region, corresponding to charge transfer resistance (Rct) at the electrode–electrolyte interface and Na⁺ diffusion process in the electrode, respectively. Fresh Fe₈CoSe₄@NC exhibits a significantly smaller Rct state (10.56 Ω) than that of fresh Fe₈NiSe₄@NC (35.25 Ω) due to the higher percentage of the smaller pore size and more complete electrolyte penetration for Fe₈CoSe₄@NC than the Fe₈NiSe₄@NC electrode, as revealed using a BET measurement (Figure 1c,d) [46]. After the first cycle, the Rct values of Fe₈CoSe₄@NC and Fe₈NiSe₄@NC decreased to 4.63 and 6.52 Ω, respectively, and a much larger variation of the Rct values for Fe₈NiSe₄@NC was observed, indicating a more robust structure of Fe₈CoSe₄@NC than Fe₈NiSe₄@NC. This observation is in agreement with the results obtained from CV scans. On the other hand, the slope of the slanted line
observed in the low-frequency region represents the Warburg impedance ($Z_w$) associated with the diffusion of Na\(^+\) \cite{47,48}. It is apparently observed that the slope of Fe\(_2\)CoSe\(_4\)@NC is much higher than that of Fe\(_2\)NiSe\(_4\)@NC after the first charge/discharge cycle. This indicates a faster Na\(^+\) diffusion rate in the former electrode than the latter one, and also that the crystalline structure of Fe\(_2\)CoSe\(_4\)@NC is more conductive for Na\(^+\) diffusion than Fe\(_2\)NiSe\(_4\)@NC, which is probably due to the larger interplanar distance of Fe\(_2\)CoSe\(_4\)@NC than Fe\(_2\)NiSe\(_4\)@NC, as observed in HRTEM.

The rate capability of Fe\(_2\)CoSe\(_4\)@NC and Fe\(_2\)NiSe\(_4\)@NC was evaluated by varying the current densities from 0.1 to 10 A g\(^{-1}\), as depicted in Figure 5a. Fe\(_2\)CoSe\(_4\)@NC demonstrates a reversible specific capacity of 470, 378, 362, 326, and 270 mAh g\(^{-1}\) at a current density of 0.1, 0.5, 1, 2, 5, and 10 A g\(^{-1}\), respectively. Similarly, Fe\(_2\)NiSe\(_4\)@NC exhibits rate capability, delivering 530, 330, 318, 315, 300, and 270 mAh g\(^{-1}\)-specific capacities at the current densities of 0.1, 0.5, 1, 2, 5, and 10, respectively. It is observed that Fe\(_2\)CoSe\(_4\)@NC exhibits a lower reduction in capacity than Fe\(_2\)NiSe\(_4\)@NC with an increase in current density, possibly due to the more robust structure of the former than the latter, which surpasses that of most single transition metal selenides reported in the literature, as illustrated in Figure 5b and Table S1.

As illustrated in Figure 5c, the Fe\(_2\)CoSe\(_4\)@NC electrode delivers a specific discharge capacity of 352 mA h g\(^{-1}\) after 2100 cycles at 1.0 A g\(^{-1}\), much higher than that of Fe\(_2\)NiSe\(_4\)@NC (282.2 mA h g\(^{-1}\)). Fe\(_2\)CoSe\(_4\)@NC and Fe\(_2\)NiSe\(_4\)@NC maintain capacities of 380 and 340 mA h g\(^{-1}\) (Figure S5) after 1500 cycles with a current density of 2 A g\(^{-1}\) (Figure S5). At a current density of 4 A g\(^{-1}\), the capacities of the Fe\(_2\)CoSe\(_4\)@NC and Fe\(_2\)NiSe\(_4\)@NC electrodes retain 370 and 310 mA h g\(^{-1}\) after 900 cycles, respectively (Figure S6). This indicates that the Fe\(_2\)CoSe\(_4\)@NC electrode possesses a higher energy density and cycle stability than Fe\(_2\)NiSe\(_4\)@NC.

![Figure 5. Electrochemical performance of Fe\(_2\)CoSe\(_4\)@NC and Fe\(_2\)NiSe\(_4\)@NC. (a) Rate performances at current densities from 0.1 to 10 A g\(^{-1}\) and (c) cycling performances at a current density of 1 A g\(^{-1}\) of Fe\(_2\)CoSe\(_4\)@NC and Fe\(_2\)NiSe\(_4\)@NC. The Coulombic efficiency (CE, orange line) is closing to 100%, as shown in the right axis and directed by the orange arrow. (b) Rate capability of Fe\(_2\)CoSe\(_4\)@NC and those of reported single transition metal selenides electrodes, as cited in supporting information \cite{29,42,49–63}.

As illustrated in Figure 5c, the Fe\(_2\)CoSe\(_4\)@NC electrode delivers a specific discharge capacity of 352 mA h g\(^{-1}\) after 2100 cycles at 1.0 A g\(^{-1}\), much higher than that of Fe\(_2\)NiSe\(_4\)@NC (282.2 mA h g\(^{-1}\)). Fe\(_2\)CoSe\(_4\)@NC and Fe\(_2\)NiSe\(_4\)@NC maintain capacities of 380 and 340 mA h g\(^{-1}\) (Figure S5) after 1500 cycles with a current density of 2 A g\(^{-1}\) (Figure S5). At a current density of 4 A g\(^{-1}\), the capacities of the Fe\(_2\)CoSe\(_4\)@NC and Fe\(_2\)NiSe\(_4\)@NC electrodes retain 370 and 310 mA h g\(^{-1}\) after 900 cycles, respectively (Figure S6). This indicates that the Fe\(_2\)CoSe\(_4\)@NC electrode possesses a higher energy density and cycle stability than Fe\(_2\)NiSe\(_4\)@NC.
To further elucidate the exceptional rate performance of the Fe$_2$CoSe$_4$@NC electrode, CV scans at sweep rates from 0.2 to 1.0 mV s$^{-1}$ were conducted to differentiate pseudocapacitive and diffusion-controlled contributions to energy storage capacity. As shown in Figure 6a, the CV profiles reveal two distinct pairs of cathodic and anodic peaks. The current response to the scan rate follows the relationship described below (Formulas (8) and (9)):

\[ i = ai^b \]  (8)

\[ \log(i) = b \log(v) + \log(a) \]  (9)

where a and b represent adjustable parameters. At b = 0.5, diffusion-controlled behavior prevails during the charge/discharge process, whereas when b = 1, the pseudocapacitive effect dominates. In the current study, the b values of the three reduction peaks (peaks 1, 2, and 3) and the corresponding oxidation peaks (peaks 4, 5, and 6) were determined to be 0.77, 0.97, 0.91, 0.85, 0.97, and 0.91, respectively, by log(i) versus log(v) plots (Figure 6b). These values are all between 0.6 to 1.0, indicating that the electrochemical reactions of the Fe$_2$CoSe$_4$@NC electrode are dominated by both diffusion-controlled and pseudocapacitive behaviors at a fixed voltage, which can be calculated following Equation (10):

\[ i(V) = k_1 \times v + k_2 \times v^{1/2} \]  (10)

where $k_1 \times v$ and $k_2 \times v^{1/2}$ represent the pseudocapacitive capacity and diffusion-controlled capacity, respectively. As summarized in Figure 6c, the pseudocapacitive contribution was estimated to be 90.6%, 92.1%, 93.6%, 94.5%, and 95.7% at the scan rates of 0.2, 0.4, 0.6, 0.8, and 1.0, respectively, showing a continuous increase in pseudocapacitive contribution to energy storage of Fe$_2$CoSe$_4$@NC with increasing scan rate. As expected, the pseudocapacitive contribution dominates the charge-storage capacity at higher scan rates, which is beneficial for fast Na$^+$ transfer kinetics during the intercalation/extraction process [8]. Additionally, Figure 6d further illustrates the detailed pseudocapacitive portion (blue region) in comparison with the total current measured at a scan rate of 1.0 mV s$^{-1}$.

![Figure 6](image_url)

**Figure 6.** (a) CV curves at scan rates from 0.2 to 1 mV s$^{-1}$; (b) plots of log(v) versus log(i); (c) capacitive (light blue bars) and diffusion-controlled (light green bars) contribution at different scan rates; and (d) capacitive contribution (light blue shadow) at 1 mV s$^{-1}$ for the Fe2CoSe4@NC electrode.
3. Materials and Methods

3.1. Chemicals
Iron (III) nitrate (Fe(NO$_3$)$_3$·9H$_2$O), cobalt nitrate hexa-hydrate (Co(NO$_3$)$_3$·6H$_2$O) and nickel nitrate hexa-hydrate (Ni(NO$_3$)$_3$·6H$_2$O) were purchased from Damao Chemical Reagents Factory (Tianjin, China). N, N-dimethylformamide (DMF), selenium powder, trimesic acid, polyvinylpyrrolidone (PVP), and ethanol were purchased from Energy Chemical Co (Beijing, China). H$_2$/Ar (10 vol% H$_2$) were obtained from Guangzhou Messer Gas (Guangzhou, China). Deionized (DI) water was obtained from a Barnstead Nanopure water purification system (18.3 MΩ·cm, Thermo Fisher Scientific, MA, USA). All chemicals were used without further purification.

3.2. Synthesis of FeCo-MOFs and FeNi-MOFs
In a typical process, Fe(NO$_3$)$_3$·9H$_2$O (4.5 mmol) and Co(NO$_3$)$_3$·6H$_2$O, (1.5 mmol) were added to a mixed solution of ethanol, DMF, and DI water (20 mL, 20 mL, and 20 mL) under vigorous stirring for about 10 min. Simultaneously, 1.5 mmol of trimesic acid and 3 g of PVP were dissolved in the same mixed solution under vigorous stirring for about 30 min. The resulting solution was then transferred into a 100 mL Teflon-lined autoclave, heated to 150 °C, and maintained for 10 h. The product was cooled to room temperature and washed three times with ethanol and DMF to obtain a metal organic framework containing iron and cobalt metal centers (denoted as FeCo-MOFs). FeNi-MOFs was also prepared using a similar protocol, with the molar ratio of iron nitrate Fe(NO$_3$)$_3$·9H$_2$O to Ni(NO$_3$)$_3$·6H$_2$O being 1 mmol:1 mmol. All other conditions remained the same.

3.3. Synthesis of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC
The FeCo-MOFs and FeNi-MOFs precursors were well ground with selenium powder (in weight ratio 1:2), placed in a silica-glazed ceramic boat, and covered with Cu foil. Selenization was carried out at 300 °C for 4 h under H$_2$/Ar (10 vol% H$_2$), with a ramping rate of 2 °C min$^{-1}$. The temperature was heated to, and maintained at, 700 °C for 2 h for the carbonization of MOFs. Finally, the obtained samples are denoted as Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC.

3.4. Materials Characterization
X-ray diffraction (XRD) was performed on a Bruker D8 Advance (Billerica, MA, USA) using Cu-K$_\alpha$ radiation ($\lambda$ = 1.5406Å). Thermal gravimetric analysis (TGA) was conducted on Mettler Toledo TGA/SDTA851 (Zurich, Switzerland) in an O$_2$ atmosphere at a heating rate of 5 °C min$^{-1}$. Nitrogen adsorption–desorption isotherms were acquired at 77 K with an Autosorb-iQ automatic volumetric instrument (Anton Paar, Graz, Austria). X-ray photoelectron spectroscopy (XPS) was acquired with a Phi X-tool instrument (Kanagawa, Japan). The microstructure and morphology of the samples were examined using field-emission scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan) and high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2010, Tokyo, Japan).

3.5. Coin Cell Assembly
A slurry-coating procedure was adopted for the preparation of the working electrode as follows. Firstly, a homogeneous slurry was prepared by mixing Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC, carbon black (Super P, Timcal, Bironico, Switzerland), and sodium alginate binder at a mass ratio of 8:1:1, evenly pasted onto a copper foil by applying a film applicator, and was dried at 70 °C in an electric oven overnight in order to remove the solvent. The mass loading of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC was about 1.2–1.5 mg·cm$^{-2}$ on each electrode.

The coin cells of CR2032-type were built in an argon-filled glove box (Vigor-LG2400/750TS, LTD, Suzhou, China), in which the oxygen and water contents were less than 1 ppm. SIBs were assembled with a sodium tablet and glass fiber as counterpart electrode and separator.
respectively. A Celgard-2400 film was used as a separator. The recipe of the commercial electrolyte is 1.0 M NaCF$_3$SO$_3$ in diglyme.

3.6. Electrochemical Measurements

The electrochemical properties of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC as anodes of SIBs was tested using CR2032 coin cells. The galvanostatic discharge/charge (GCD) measurements were tested on a battery analysis system (CT2001A, LAND). Cyclic voltammetry (CV) tested at a scan rate of 0.2 mV s$^{-1}$, and electrochemical impedance spectra (EIS), conducted with the frequency range of 100 kHz to 0.01 Hz, were acquired with the CHI660 electrochemical workstation (Shanghai CH Instrument Co., Ltd., Shanghai, China).

4. Conclusions

In summary, the binary-metal selenides Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC were successfully synthesized with the preparation of a Fe/Co and Fe/Ni binary-metal organic framework using hydrothermal methods and sequential selenization binary Fe/Co and Fe/Ni MOF. The formation of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC was evidenced using XRD, XPS, and HRTEM. Fe$_2$CoSe$_4$@NC demonstrates higher long-term cycling stability and rate performance than Fe$_2$NiSe$_4$@NC, maintaining capacities of 352 and 282.2 mAh g$^{-1}$ after 2100 cycles at 1.0 A g$^{-1}$, respectively. Such a higher electrochemical performance of Fe$_2$CoSe$_4$@NC than Fe$_2$NiSe$_4$@NC was ascribed to the higher portion of micropores and a higher diffusion rate of sodium-ions among the electrode composite. This study presents a novel method for synthesizing binary-metal selenides towards high-performance sodium-ion storage.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics12060165/s1, Figure S1: TGA patterns of (a) Fe$_2$CoSe$_4$@NC and (c) Fe$_2$NiSe$_4$@NC products of combustion in air; Figure S2: XRD spectra of (a) Fe$_2$CoSe$_4$@NC and (b) Fe$_2$NiSe$_4$@NC products of combustion in air; Figure S3: Full XPS of (a) Fe$_2$CoSe$_4$@NC and (b) Fe$_2$NiSe$_4$@NC; Figure S4: Raman of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC; Figure S5: Cycling performances of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC at a current density of 2 A g$^{-1}$; Figure S6: Cycling performances of Fe$_2$CoSe$_4$@NC and Fe$_2$NiSe$_4$@NC at a current density of 4 A g$^{-1}$; Table S1: Electrochemical rate performances of already reported metal selenide anodes.

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Conflicts of Interest: Hangxuan Xie, Wei Zhang, Chao Wang, Shangcheng Zhao, and Zhentao Hao are employed by China Southern Power Grid Technology Co., Ltd.. The remaining authors of the paper declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References


34. Muralee Gopi, C.V.V.; Reddy, A.E.; Kim, H.-J. Wearable superhigh energy density supercapacitors using a hierarchical ternary metal selenide composite of CoNiSe2 microspheres decorated with CoFe2Se4 nanorods. J. Mater. Chem. A 2018, 6, 7439–7448. [CrossRef]


36. Park, J.-S.; Chan Kang, Y. Multicomponent (Mo, Ni) metal sulfide and selenide microspheres with empty nanovoids as anode materials for Na-ion batteries. J. Mater. Chem. A 2017, 5, 8616–8623. [CrossRef]

37. He, Y.; Luo, M.; Dong, C.; Ding, X.; Yin, C.; Nie, A.; Chen, Y.; Qian, Y.; Xu, L. Coral-like NiCo1–xSe2 for Na-ion battery with ultralong cycle life and ultrahigh rate capability. J. Mater. Chem. A 2019, 7, 3933–3940. [CrossRef]


51. Huang, P.; Zhang, S.; Ying, H.; Zhang, Z.; Han, W. Few-layered Ti3C2 MXene anchoring bimetallic selenide NiCo2Se4 nanoparticles for superior Sodium-ion batteries. Chem. Eng. J. 2021, 417, 129161. [CrossRef]


53. Liang, H.; Li, X.; Liu, Z.; Yang, W.; Liu, X.; Zhang, Y.; Fan, H. In situ etching strategy to construct yolk–shell CoSe2@NiCoSe4-NC heterostructures for high-performance sodium-ion battery. Mater. Chem. Front. 2022, 6, 194–202. [CrossRef]


55. Liu, J.; Leng, Z.; Dong, H.; Xu, X.; Lv, C.; Wei, H.; Yu, L.; Yang, J.; Geng, H. In situ interface engineering of NiSe with interlinked conductive networks for high energy density sodium half/full batteries. Inorg. Chem. Front. 2023, 10, 4076–4086. [CrossRef]

57. Dong, C.; Wu, L.; He, Y.; Zhou, Y.; Sun, X.; Du, W.; Sun, X.; Xu, L.; Jiang, F. Willow-Leaf-Like ZnSe@N-Doped Carbon Nanoarchitecture as a Stable and High-Performance Anode Material for Sodium-Ion and Potassium-Ion Batteries. *Small* 2020, 16, 2004580. [CrossRef]


59. Kong, F.; Han, Z.; Tao, S.; Qian, B. Core–shell structured SnSe@C microrod for Na-ion battery anode. *J. Energy Chem.* 2021, 55, 256–264. [CrossRef]


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