

Article

Hollow-Structured Carbon-Coated $\text{Co}_x\text{Ni}_y\text{Se}_2$ Assembled with Ultrasmall Nanoparticles for Enhanced Sodium-Ion Battery Performance

Chao Wang ^{1,2}, Weijie Si ^{3,*}  and Xiongwu Kang ^{3,*} 

¹ National Institute of Guangdong Advanced Energy Storage, Guangzhou 510000, China; wangchaomly@163.com

² China Southern Power Grid Technology Co., Ltd., Guangzhou 510080, China

³ New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou 510006, China

* Correspondence: 202221047646@mail.scut.edu.cn (W.S.); esxkang@scut.edu.cn (X.K.)

Abstract: Transition metal selenides are considered one of the most promising materials for sodium-ion battery anodes due to their excellent theoretical capacity. However, it remains challenging to suppress the volume variation and the resulted capacity decay during the charge–discharge process. Herein, hollow-structured CoNiSe_2 dual transition metal selenides wrapped in a carbon shell ($\text{HS-Co}_x\text{Ni}_y\text{Se}_2@\text{C}$) were deliberately designed and prepared through sequential coating of polyacrylonitrile (PAN), ion exchange of ZIF-67 with Ni^{2+} metal ions, and carbonization/selenization. The hollow structure was evidenced by transmission electron microscopy, and the crystalline structure was confirmed by X-ray diffraction. The ample internal space of $\text{HS-Co}_x\text{Ni}_y\text{Se}_2@\text{C}$ effectively accommodated volume expansion during the charge and discharge processes, and the large surface area enabled sufficient contact between the electrode and electrolyte and shortened the diffusion path of sodium ions for a feasible electrochemical reaction. The surface area and ionic conductivity of $\text{HS-Co}_x\text{Ni}_y\text{Se}_2@\text{C}$ were strongly dependent on the ratio of Co to Ni. The synergistic effect between Co and Ni enhanced the conductivity and electron mobility of $\text{HS-Co}_x\text{Ni}_y\text{Se}_2@\text{C}$, thereby improving charge transfer efficiency. By taking into account the structural advantages and rational metal selenide ratios, significant improvements can be achieved in the cycling performance, rate performance, and overall electrochemical stability of sodium-ion batteries. The optimized $\text{HS-Co}_x\text{Ni}_y\text{Se}_2@\text{C}$ demonstrated excellent performance, and the reversible capacity remained at 334 mAh g^{-1} after 1000 cycles at a high current of 5.0 A g^{-1} .

Keywords: sodium-ion battery; hollow structure; binary transition metal selenides; synergistic effect



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1. Introduction

With the increasing share of intermittent renewable energy sources, advancing high-performance energy storage technologies has become a critical focus for the scientific community. Due to the abundance and low cost of sodium resources, sodium-ion batteries (SIBs) have attracted significant attention as an alternative to conventional lithium-ion battery systems (LIBs). However, the larger ionic radius of Na^+ compared to that of Li^+ leads to substantial volume changes in electrode materials and slower ion diffusion kinetics, resulting in poor cycling stability and rate performance for the well-developed electrode

materials in LIBs [1]. Thus, it is desirable to design and develop novel electrode materials for the practical application of SIBs [2,3]. Many advanced anode and cathode materials have been developed through strategies such as nanostructure engineering and alloy design to enhance structural stability and ionic conductivity, thereby improving cycling performance and rate capability [4,5].

Transition metal selenides (TMSs) have demonstrated significant potential as anode materials for sodium-ion batteries owing to their excellent electrical conductivity, high theoretical specific capacity, favorable electrochemical properties, and structural stability [6]. The weak M–Se bonds facilitate conversion reactions, enhancing cycling performance. Men et al. [7] have proposed novel porous FeSe₂ composites wrapped in an N-doped porous carbon framework (P–FeSe₂/NCF) through a scalable pyrolysis method, which retains abundant porosity and a dodecahedral structure embedded with carbon nanotubes. Even at relatively high current densities of 5 and 10 A g^{−1}, the porous FeSe₂ anode maintains capacities of 548 and 466 mAh g^{−1}, respectively. Such excellent rate performance has been ascribed to the unique porous structure and large surface area. Compared to monometallic selenides, bimetallic selenides exhibit electronic coupling and synergistic effects between their components, which may produce more ion defects and an ion diffusion path, thus further enhancing ion diffusion rates. Weng et al. [8] synthesized a bimetallic heterojunction selenide (CoSe₂/NiSe₂@N–C) using a Co/Ni-ZIF template, with the selenide grown within N-doped carbon nanofibers. The enhanced performance of this binary transition metal selenide was ascribed to the built-in electric field at the interface of the two TMSs.

In addition, nanostructure engineering has demonstrated an excellent strategy in the development of high-performance anode materials. Among the alloy anodes for sodium-ion batteries, yolk-shell and hollow structures often outperform the solid-state counterpart due to the enhanced large surface area of the contacting electrolyte and offering more abundant reactive sites [9]. Additionally, hollow and yolk-shell structures effectively mitigate the volume changes induced by the insertion and extraction of sodium ions during the charge–discharge process and enhance the robustness against the fragmentation of the nanostructure of the electrode towards a long lifespan. Furthermore, unlike in the solid-state counterpart, the formation of a hollow structure offers shorter ion transport pathways and facilitates the rapid insertion and extraction of sodium ions, improving the rate performance and enabling the battery to maintain high capacity and efficiency under high-rate conditions. Zhou et al. [8] employed an ion-exchange method to anchor hollow- and hetero-structured ZnSe/NiSe₂ bimetallic selenides (V-ZnSe/NiSe₂@H-NC). Owing to the unique hollow and hetero structure, it exhibited excellent performance as an anode material for sodium-ion batteries, achieving a capacity of 314 mAh g^{−1} at a current density of 2.0 A g^{−1} after 2000 cycles.

Currently, most studies focus on structural design and the introduction of metals ions into the parent metal selenide to enhance the overall electrochemical performance. However, the impact of varying the metal ratios on material performance has received limited attention, especially in the porous structure counterpart. Therefore, the simultaneous introduction of multiple metals with varying ratios during the synthesis of hollow-structured TMSs along with a systematic study of how variations in metal content influence performance, remains an under-explored research area. Such investigations could not only deepen our understanding of metal ratio optimization in enhancing electrochemical behavior but also offer new insights and guidance for the design of advanced energy storage materials.

Inspired by the aforementioned studies, we developed a hollow-structured, carbon-encapsulated Co/Ni bimetallic transition metal selenide (CoNi-Se@C) as a multifunctional anode material for sodium-ion batteries, using ZIF-67 as a sacrificial template through a

straightforward PAN encapsulation and ion-exchange process. Although binary metal selenides of Co with Mn, Cu, and Fe were also explored, achieving a hollow structure remains challenging. The experimental results revealed that with increasing Ni content, the electrochemical performance initially improved but then declined, and the best performance was achieved at the ratio of Co:Ni = 1.05:0.95, possibly ascribing to the highest electrochemical surface area and ion conductance due to the optimized synergistic effects between the two metal components [10]. The hollow CoNi-Se@C with optimized Ni/Co ratio exhibited a specific discharge capacity of 334 mAh g⁻¹ after 1000 cycles at a high current of 5.0 A g⁻¹, and a high discharge capacity of 428 mAh g⁻¹ at a high current of 5.0 A g⁻¹, demonstrating excellent commercial potential.

2. Results

Figure 1a illustrates the synthesis scheme of the CoNi-Se@C material. First, a ZIF-67 precursor was prepared by coordinating Co²⁺ ions and 2-methylimidazole in methanol. Then, a simple “phase separation method” was employed to uniformly coat ZIF-67 with polyacrylonitrile (PAN) [11], which served as the primary carbon source, resulting in the ZIF-67@PAN precursor. Subsequently, the obtained ZIF-67@PAN was dispersed in ethanol and subjected to ion exchange with Ni²⁺ for 2 h. This process partially etched the inner ZIF-67, transforming it into a hollow layered double hydroxide (LDH) structure [12], yielding Co_xNi_y-LDH@PAN. Afterward, the dried Co_xNi_y-LDH@PAN was mixed with Se powder at a 1:1 mass ratio, placed in an alumina boat, and annealed under an Ar/H₂ atmosphere at 500 °C for 6 h. Following this high-temperature selenization process, hollow-structured Co_xNi_ySe₂@C was obtained and denoted as CoNi-Se@C. The ratio of Co to Ni was determined to be 0.51:0.49 by inductively coupled plasma optical emission spectroscopy (ICP-OES), and the chemical formula was denoted as Co_{0.51}Ni_{0.49}Se₂, as shown in Table S1, which was consistent with that determined by XPS (Table S2). The counterparts with varied ratios of Ni to Co were obtained via ion exchange for 1 h and 3 h, and are denoted as CoNi-1-Se@C and CoNi-3-Se@C. The formulas of Co_xNi_ySe₂ were determined to be Co_{0.59}Ni_{0.42}Se₂, Co_{0.56}Ni_{0.5}Se₂, and Co_{0.59}Ni_{0.59}Se₂ for CoNi-1-Se@C, CoNi-Se@C, and CoNi-3-Se@C, respectively, indicating that Ni content was consistently increasing with the prolonged Ni²⁺ exchange course.

As shown in Figure 1b,c, after high-temperature selenization, the obtained CoNi-Se@C material showed a polyhedral shape, smooth surface, and intact structure. The size of the polyhedron was approximately from 500 to 700 nm. The hollow structure of CoNi-Se@C is observed in Figure 1d. This hollow structure not only helps mitigate mechanical stress caused by volume expansion during charge and discharge but also increases the specific surface area, providing more active sites for sodium-ion storage, thereby enhancing the electrochemical performance of the material.

In addition, the high-resolution transmission electron microscopy (HRTEM) images in Figure 1e indicate that the shell of CoNi-Se@C was assembled with nanoparticles from 3 to 7 nm. The nano-sized nanoparticles display large surface area and offer abundant active sites for reaction and the pores among them favor the penetration of electrolytes and promote electrochemical reaction. Figure 1f displays the distinct lattice fringes with spacing of 0.271 and 0.265 nm, corresponding precisely to the (1,0,1) and (0,0,2) reflection of CoNiSe₂. Meanwhile, the selected area electron diffraction (SAED) pattern in Figure 1g presents multiple clear diffraction rings, which match well with the (0,0,2), (0,1,2), (0,0,3), and (−1,2,2) planes of CoNiSe₂, further verifying the crystalline structure of the material. Furthermore, the elemental mapping in Figure 1h–m shows a uniform distribution of Co, Ni, Se, N, and C elements within the CoNi-Se@C material, indicating the formation of uniform binary Co/Ni diselenide.

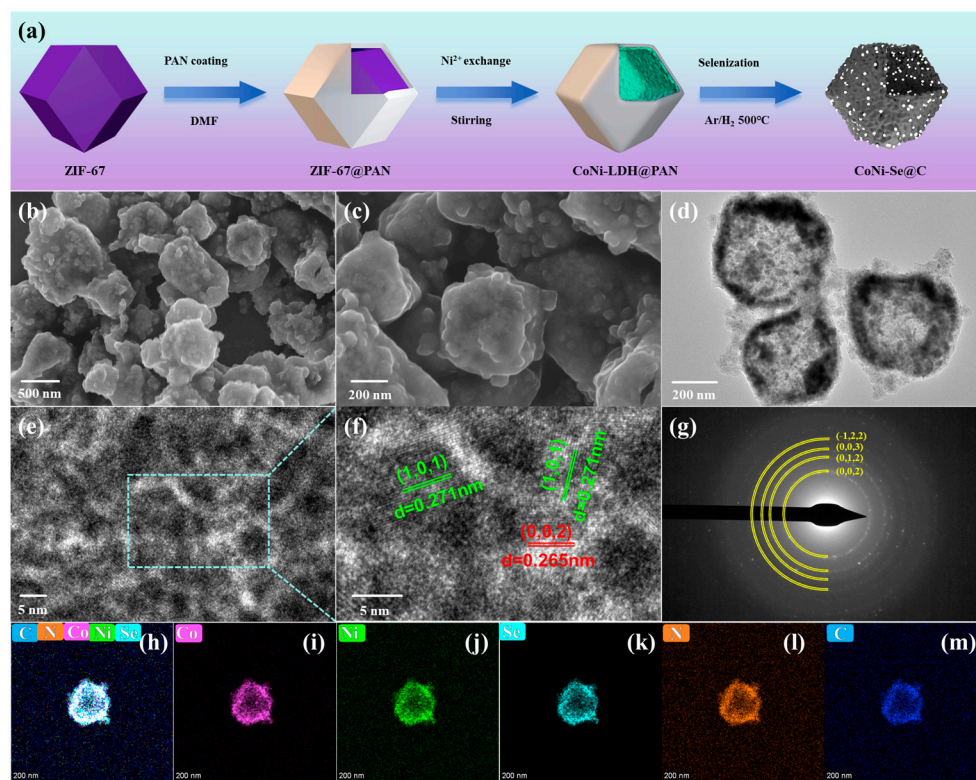


Figure 1. (a) Schematic illustration CoNi-Se@C synthesis. (b,c) SEM images, (d) TEM image, (e,f) HRTEM images, and (g) SAED pattern of CoNi-Se@C. (h–m) Element mapping images of Co, Ni, Se, N, and C.

Figure 2a presents the XRD pattern of CoSe₂@C, revealing that without ion exchange, the direct selenization of pure ZIF-67@PAN at 500 °C yielded CoSe₂. In contrast, the XRD patterns of CoNi-Se@C, CoNi-1-Se@C, and CoNi-3-Se@C showed a high degree of correspondence with the reference pattern of CoNiSe₂ (PDF#89-7162). This indicates that selenization at 500 °C resulted in the formation of a Co_xNi_ySe₂ (Figure 2b), and the change of the ratio of Co²⁺ to Ni²⁺ did not change the lattice parameter of Co_xNi_ySe₂. Additionally, the Raman spectra of CoNi-Se@C showed an apparent defect and graphitic bands with an I_D/I_G ratio of 1.15, indicating the presence of defects and disordered carbon structures, which contributed to enhanced electron transport and electrochemical activity (Figure S1).

The N₂ adsorption/desorption isotherms were employed to analyze the changes in the specific surface area of the samples and to further investigate the impact of Ni²⁺ incorporation on the structure. All four samples exhibited typical type IV adsorption behavior, with a pore size of approximately 4.5 nm (Figure 2c,d) [13]. The surface areas for CoSe₂@C, CoNi-1-Se@C, CoNi-Se@C, and CoNi-3-Se@C were calculated to be 93.72, 120.4, 168.15, and 131.87 m² g^{−1}, respectively, using the Brunauer–Emmett–Teller (BET) method. It indicates that the progressive introduction of Ni²⁺ promoted the formation of hollow structures, leading to an initial increase and further decline in surface area. The initial increase of the surface area of CoNi-Se@C with progressive ion exchange could be attributed to the creation of the hollow structure and increased cavity. However, when the ion exchange time extend to 3 h, collapse and contraction of the hollow structure may occur during selenization, which may ultimately decrease the specific surface area [14].

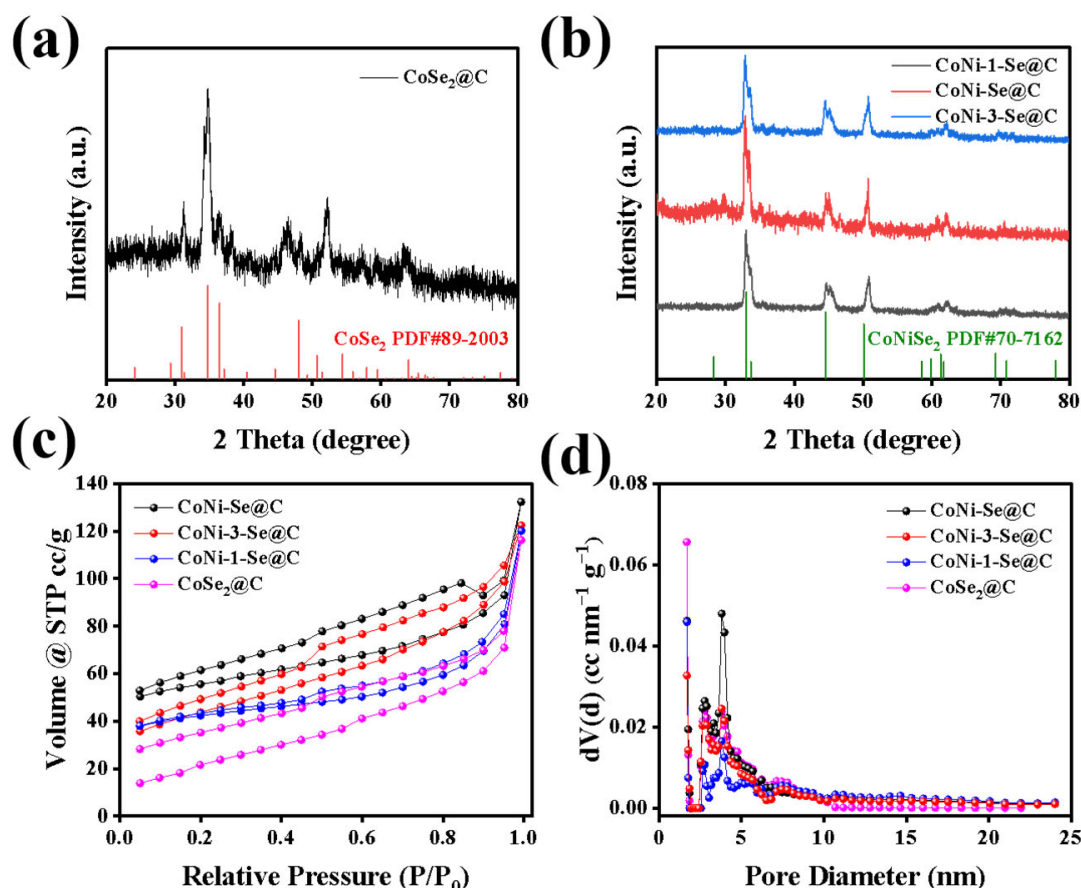


Figure 2. XRD patterns of (a) $\text{CoSe}_2@\text{C}$, (b) CoNi-Se@C , CoNi-1-Se@C , and CoNi-Se-3@C . (c) Nitrogen adsorption/desorption isotherm and (d) pore size distributions of CoNi-Se@C , CoNi-1-Se@C , CoNi-Se-3@C , and $\text{CoSe}_2@\text{C}$.

As shown in Figure 3a, the XPS survey spectrum clearly revealed the presence of Co, Ni, Se, N, and C. First, Figure 3b presents the high-resolution spectrum of Co 2p. The two strong spin-orbit coupling peaks located at 794.5 eV and 779.3 eV were indexed to $\text{Co}^{2+} 2p_{1/2}$ and $\text{Co}^{2+} 2p_{3/2}$. The two satellite peaks (Sat.) were located at 803.9 eV and 784.9 eV, individually. Additionally, two Co–O peaks were observed at binding energies of 797.9 eV and 781.4 eV, which can be attributed to surface oxidation of the sample [15,16]. In Figure 3f, the characteristic peaks of $\text{Ni}^{2+} 2p_{1/2}$ and $\text{Ni}^{2+} 2p_{3/2}$ were observed at 870.27 eV and 852.0 eV, and the satellite peaks were located at 859.5 eV and 878.5 eV, respectively. Similarly, corresponding Ni–O peaks are also present in the Ni 2p spectrum (873.9 eV and 854.4 eV) [17,18]. Furthermore, Figure 3d shows the high-resolution spectrum of Se 3d. Se exhibited two peaks at 53.8 eV and 52.8 eV, which were indexed to $\text{Se}^{2-} 3d_{3/2}$ and $\text{Se}^{2-} 3d_{5/2}$, respectively. The characteristic peak at 57.8 eV is attributed to SeO_2 [19–21]. The high-resolution N 1s spectrum (Figure 3e) identifies three nitrogen types: pyridinic N (397.1 eV), pyrrolic N (397.7 eV), and graphitic N (398.9 eV) [22]. Meanwhile, the C 1s spectrum (Figure 3f) displays three characteristic peaks at 289.1, 286.7, and 284.8 eV, corresponding to C–O, C–N, and C–C/C=C bonds, respectively [23].

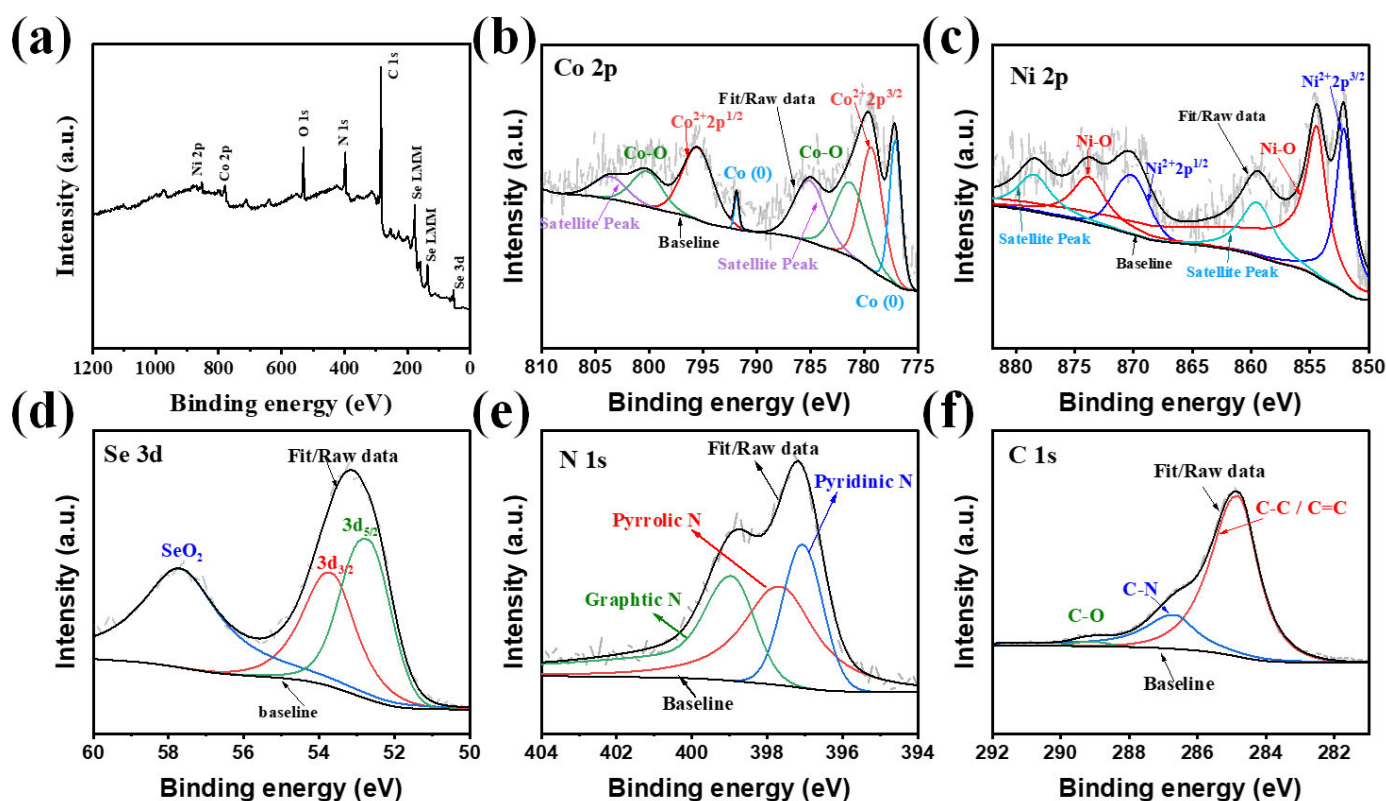


Figure 3. (a) Full survey XPS spectrum and (b–f) high-resolution XPS spectra of Co 2p, Ni 2p, Se 3d, N 1s, and C 1s of CoNi-Se@C.

The cyclic voltammetry (CV) curves of the CoNi-Se@C material with varied ratios of Co to Ni and CoSe₂ assembled with a sodium metal anode, measured over the voltage range from 0.01 to 3.0 V for the first three cycles, are shown in Figures 4a and S2. In the first cycle of CV scan for CoNi-Se@C (Figure 4a), a distinct reduction peak was observed at around 0.9 V, ascribing to the formation of the solid electrolyte interface (SEI) layer and the initial insertion of Na⁺ ions [7]. In the subsequent second and third cycle, the high degree of overlap between the CV curves demonstrated the excellent cycling stability of the CoNi-Se@C electrode after initial activation [1,24]. These results highlight the potential of the CoNi-Se@C material for sodium-ion batteries, particularly its ability to maintain superior electrochemical performance and stability over extended cycling. In the cathodic scan, the reduction peaks were sequentially observed at 1.357, 1.071, and 0.677 V, and a single oxidation peak was observed at 1.925 V, which were possibly attributed to the specific sodiation and desodiation reactions or pseudocapacitive behavior [8,25]. To this end, XRD analysis was performed on CoNi-Se@C in the fully discharged state to investigate the phase evolution of the material. The results showed the appearance of characteristic diffraction peaks of Na₂Se and Ni/Co (Figure S3), indicating a phase transition of Co_xNi_ySe₂ to metallic Co/Ni and Na₂Se by Na⁺ insertion [26]. The possible reactions (Equations (1)–(4)) contributed to the capacity are shown below:

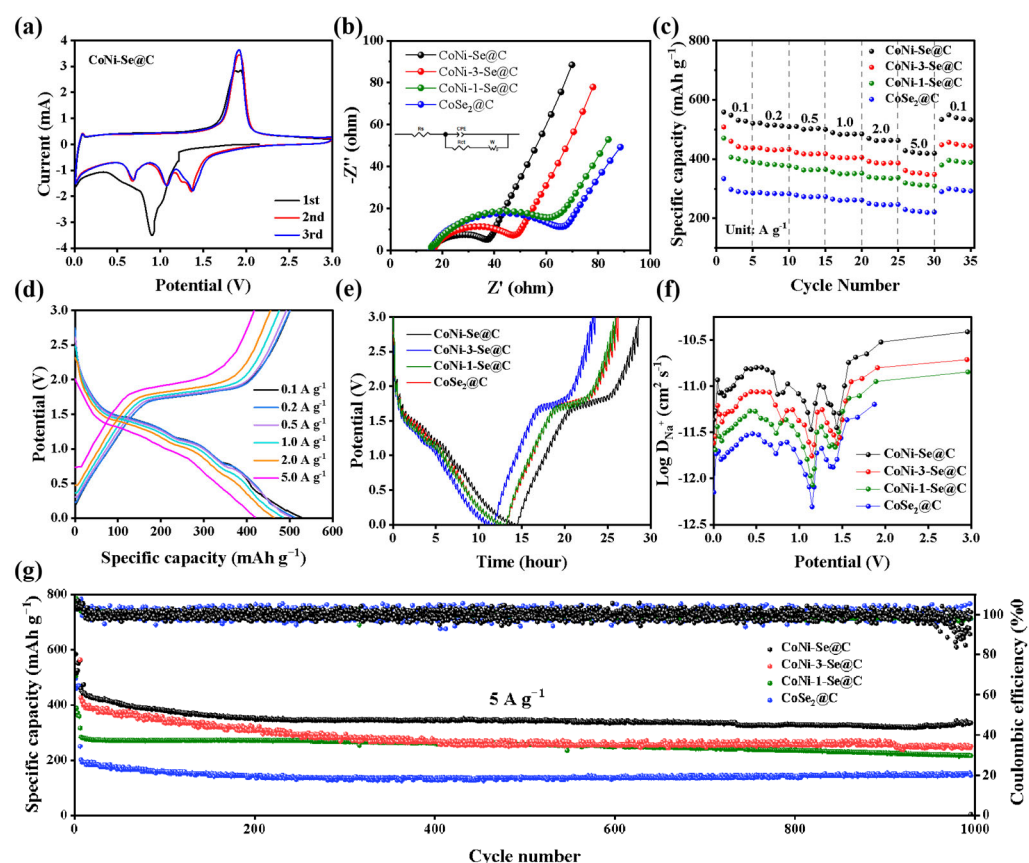
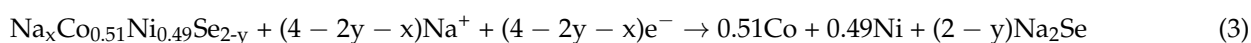
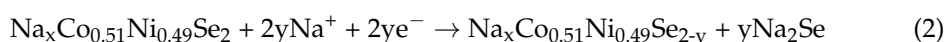
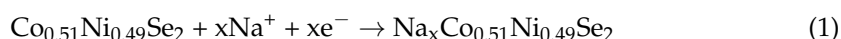
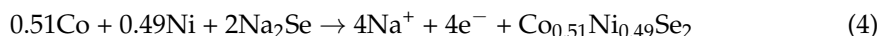


Figure 4. (a) CV curves for the first 3 cycles of CoNi-Se@C at 1.0 mV s^{-1} . (b) EIS Nyquist plots and equivalent circuit in the inset, (c) rate performances of CoSe₂@C, CoNi-1-Se@C, CoNi-Se@C, and CoNi-3-Se@C. (d) Discharge-charge curves at various rates of CoNi-Se@C. (e) GITT curves, (f) Na⁺ diffusion coefficient in discharge process and (g) long-life cycling performance at 5 A g^{-1} of CoSe₂@C, CoNi-1-Se@C, CoNi-Se@C, and CoNi-3-Se@C.

Discharge



Charge



Similar redox peaks were also observed for other anode materials of CoSe₂@C, CoNi-1-Se@C, and CoNi-3-Se@C. The related redox potentials and polarization derived are listed in Table S3. In the first scan, the cathodic peak potential for CoNi-1-Se@C was the highest among the three samples. This redox peak is related to the formation of SEI, and the highest potential indicates the earliest formation of an SEI film and protection of the electrode materials during the initial discharging process. With the increasing content of Ni in Co_xNi_ySe₂@C, the potential of the cathodic peak1 in the second cycle increased first, achieved the highest for CoNi-Se@C, and then declined considerably for CoNi-3-Se@C. The anodic peak potential in the second cycle increased consistently with the increasing of Ni content, which resulted in the consistent increase of the polarization.

Electrochemical impedance spectroscopy (EIS) with a bias of 2.4 V and amplitude of 0.05 V was employed to evaluate the impedance of different materials. Figures 4b and S4 show the Nyquist plots and fitting curves of the four materials using the equivalent circuit (inset in Figure 4b), respectively, where R_{ct} , R_s , W , and CPE represent the interfacial charge transfer resistance, solution resistance, Warburg impedance, and impedance of the constant phase element, respectively [27]. The detailed fitting parameters are shown in Table S4. R_{ct} exhibited a trend of first decreasing and then increasing with the introduction of Ni^{2+} (R_{ct} : 50.39 $\rightarrow$ 44.05 $\rightarrow$ 21.21 $\rightarrow$ 31.47 Ω), consistent with the variation of the surface area. The increases in the surface area of material resulted in more active sites, which enhanced the interfacial contact between the electrolyte and electrode, facilitating Na^+ transport and charge transfer.

The impedance of the constant phase element describes non-ideal capacitive behavior related to a rough or porous interface, varied thickness of film layer, or non-uniform reaction dynamics [28], and the variation of CPE-T and CPE-P might be caused by the roughness and porosity of the electrode materials with varied ratios of Co to Ni. It was also observed that CoNi-Se@C exhibited the highest CPE-T. The former might be related to the highest pseudocapacitance contribution of CoNi-Se@C among the three samples. The Warburg element models ion transport impedance across an electrode layer to the surface of a current collector [29]. The lowest W-R indicates the highest Na^+ diffusion rate and most accessible of Na^+ to and from the electrode surface. Additionally, the synergistic effect between Ni and Co improves electronic conductivity, further optimizing charge transport during cycling [30,31]. However, excessive Ni^{2+} content causes contraction of the hollow space and condensation of the shell, which reduces the electrochemical surface area and impairs ion transport efficiency. Therefore, precise control of Ni^{2+} doping is crucial to achieving optimal electrochemical performance by balancing improved conductivity and stability [32,33].

Figure 4c compares the rate performance of $CoSe_2@C$, CoNi-1-Se@C, CoNi-Se@C, and CoNi-3-Se@C across a current range of 0.1–5.0 A g^{-1} . Among them, CoNi-Se@C exhibited the best electrochemical performance, maintaining a high discharge capacity of 428 mAh g^{-1} even at a high current of 5.0 A g^{-1} , indicating excellent rate capability and fast charge–discharge ability. Figures 4d and S5 further present the charge–discharge curves of CoNi-Se@C under different current densities. The material consistently maintains stable charge–discharge plateaus at various rates, demonstrating superior structural stability and good reversibility, making it more suitable for high-rate charge–discharge applications compared to other materials.

To further investigate the effect of Ni content on the performance of those materials, galvanostatic intermittent titration technique (GITT) testing was conducted to explore the Na^+ diffusion rate in each material (Figure 4e). Based on the results from GITT testing, the diffusion coefficient of Na^+ can be calculated using Fick's second law with the following equation [34,35]:

$$D_{Na^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B S} \right)^2 \left(\frac{\delta E_s}{\delta E_\tau} \right)^2 \quad (5)$$

where τ is the relaxation time (s), m_B is the mass of the electrode material, V_m is the molar volume of the active material, M_B is the molar mass of the electrode material, S is the electrode area, ΔE_s represents the potential change between two consecutive relaxation periods, and ΔE_τ denotes the potential change between the static and equilibrium states. The results in Figure 4f show that CoNi-Se@C, with a Co to Ni ratio close to 1:1, exhibited a higher sodium-ion diffusion rate compared to that of other samples. For instance, the diffusion coefficient of Na^+ (D_{Na^+}) of $CoSe_2@C$, CoNi-1-Se@C, CoNi-Se@C, CoNi-3-Se@C at 0.5 V vs. Na^+/Na was approximately 3.0×10^{-12} , 4.3×10^{-12} , 1.58×10^{-11} , 8.7×10^{-12} $cm^2 s^{-1}$,

which was in the order of $\text{CoNi-Se@C} > \text{CoNi-3-Se@C} > \text{CoNi-1-Se@C} > \text{CoSe}_2\text{@C}$. The trend of Na^+ diffusion rate aligned with the previously discussed findings—initially increasing and then decreasing with the increasing ratio of Ni to Co. This phenomenon can be attributed to the partial substitution of Co^{2+} by an appropriate amount of Ni^{2+} , which exhibits the optimized synergistic interactions between the two metals, thereby achieving the highest electronic and ionic conductivity [36].

Figure 4g presents the long-term cycling performance of $\text{CoSe}_2\text{@C}$, CoNi-1-Se@C , CoNi-Se@C , and CoNi-3-Se@C at a current density of 5.0 A g^{-1} . It is evident that CoNi-Se@C exhibited the best performance, maintaining a discharge capacity of 335 mAh g^{-1} at 5.0 A g^{-1} after prolonged cycling of 1000 cycles. As shown in TEM images of CoNi-Se@C after 1000 cycles at 5.0 A g^{-1} (Figure S6), the hollow structure remained but fractures appeared, which may be related to the decline of the charge–discharge capacity. Table S5 presents a comparison of the long cycling performance of CoNi-Se@C with that of other reported metal selenides. It is evident that CoNi-Se@C exhibited excellent cycling stability and high-capacity retention over prolonged cycling. This superior performance further confirms the importance of optimizing the metal ratio for enhancing sodium storage capabilities. The synergy between Co and Ni contributes to improved structural stability, enhanced electronic conductivity, and faster ion diffusion, all of which are critical for achieving high-capacity retention and stable cycling. Conversely, inappropriate metal ratios may disrupt this synergy, leading to compromised performance.

CV tests at different scan rates ranging from 0.2 to 1.0 mV s^{-1} were conducted to investigate the contribution of the pseudo capacitance to the charge capacity of the material, and Equations (6) and (7) were utilized to calculate the contributions of pseudocapacitance and diffusion (Figures 5a,b and S7). Here, i represents the current at each peak of the CV curve, and v denotes the corresponding scan rate. In these equations, a and b serve as empirical parameters. When b approaches 0.5 , the charge/discharge process is primarily controlled by diffusion, whereas when b approaches 1 , pseudocapacitance becomes the dominant mechanism [37,38].

$$i = av^b \quad (6)$$

$$\log(i) = b \times \log(v) + \log(a) \quad (7)$$

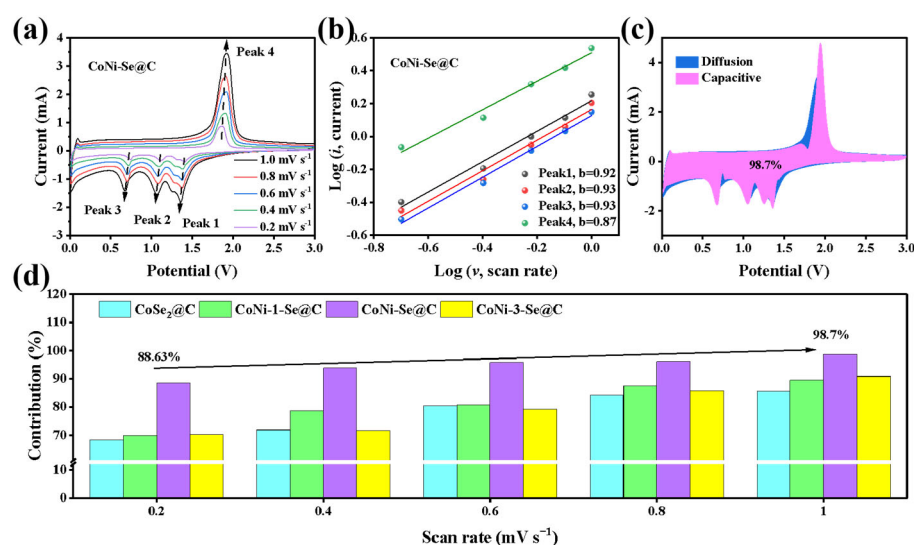


Figure 5. (a) CV curves at various scan rates. (b) The corresponding $\log(i)$ versus $\log(v)$ at each redox peak. (c) Capacitive contribution at 1.0 mV s^{-1} . (d) Contribution rates of capacitive-controlled and diffusion-controlled capacities at different scan rates.

Additionally, the contribution of pseudocapacitance can be calculated using Equation (8), where k_1v and $k_2v^{1/2}$ represent the contributions of pseudocapacitance and ion diffusion, respectively [2].

$$i(V) = k_1v + k_2v^{1/2} \quad (8)$$

As shown in Figure 5c, it was clearly demonstrated that at a scan rate of 1.0 mV s^{-1} , the contribution of pseudocapacitance predominated, highlighted in pink. Figure 5d shows the contribution of pseudocapacitance of those four samples. For CoNi-Se@C, the contribution of pseudocapacitance increased from 88.63% to 98.7% as the scan rate increased from 0.2 to 1.0 mV s^{-1} . This trend indicates that as the scan rate increased, the role of surface reactions in charge storage capacity became increasingly significant.

3. Materials and Methods

3.1. Chemicals

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole (2-MeIM), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), polyacrylonitrile (PAN), and selenium powder (Se) were all purchased from Energy Chemical Co., Ltd, Shanghai, China. N,N-Dimethylformamide (DMF), methanol, and ethanol were purchased from Damao Chemical Reagent Factory, Tianjing, China.

3.2. Synthesis of ZIF-67

In a typical synthesis, 0.04 mol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 500 mL of methanol to prepare solution A. Simultaneously, 0.16 mol of 2-methylimidazole was dissolved in 500 mL of methanol to prepare solution B. Solution A was then gradually added to solution B, and the mixture was stirred continuously for 24 h. The resulting suspension was centrifuged, and the precipitate was washed three times with methanol. Finally, the precipitate was dried at 60°C for 12 h to obtain ZIF-67.

3.3. Synthesis of ZIF-67@PAN

First, 0.5 g of ZIF-67 was evenly dispersed in 20 mL of DMF, followed by the addition of 0.5 g of PAN white powder. After stirring for 12 h, the solution was drawn into a syringe and added dropwise into stirred deionized water. The sample was collected by vacuum filtration and rinsed three times with deionized water. Finally, it was dried at 60°C for 12 h to obtain ZIF-67@PAN.

3.4. Synthesis of CoNi-1-LDH@PAN, CoNi-LDH@PAN and CoNi-3-LDH@PAN

First, 0.8 g of ZIF-67@PAN was added to 400 mL of ethanol and subjected to ultrasound for uniform dispersion, referred to as solution A. Meanwhile, 0.8 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 100 mL of ethanol to prepare solution B. Solution B was then added to solution A, and the mixture was stirred before centrifuging to collect the sample. The sample was washed three times with ethanol and dried at 60°C for 12 h to obtain CoNi-LDH@PAN. Additionally, the samples with stirring times of 1, 2, and 3 h were designated as CoNi-1-LDH@PAN, CoNi-LDH@PAN, and CoNi-3-LDH@PAN, respectively.

3.5. Synthesis of CoNi-Se@C, CoNi-1-Se@C, CoNi-3-Se@C and CoSe₂@C

The obtained CoNi-LDH@PAN was mixed with Se powder at a 1:1 mass ratio and placed in a porcelain boat. It was then annealed at 60°C under an Ar/H_2 atmosphere for 6 h (at a heating rate of 2°C min^{-1}) to obtain the CoNi-Se@C sample. Additionally, the preparation procedures for CoNi-1-Se@C, CoNi-3-Se@C, and CoSe₂@C followed the same method as described above, with the only difference being that the precursors used were CoNi-1-LDH@PAN, CoNi-3-LDH@PAN, and ZIF-67@PAN, respectively.

3.6. Materials Characterization

X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance (Berlin, Germany) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). A Phi X-tool XPS instrument from ULVAC-PHI (Kanagawa-ken, Chigasaki-shi, Japan) was used, with the standard carbon peak C1s (284.8 eV) as the calibration reference. The sample morphology was characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800, Tokyo, Japan) and transmission electron microscopy (TEM, FEI Tecnai G2 F30, Hillsboro, OH, USA). Nitrogen adsorption–desorption isotherms were measured at 77 K using an Autosorb-iQ automatic volumetric analyzer (Quantachrome, Boynton Beach, FL, USA).

3.7. Coin Cell Assembly

CoNi-Se@C, Super P, and sodium alginate were thoroughly mixed with deionized water at a mass ratio of 8:1:1 to form a black slurry. The slurry was coated onto copper foil and dried at 60 °C for 24 h in a convection oven. The resulting electrode was then cut into 13 mm diameter discs and assembled into CR-2032 coin cells. Metallic sodium was used as the counter electrode, glass fiber (Whatman GF/D, Maidstone, UK) as the separator, and 1.0 M NaCF₃SO₃ in diethylene glycol dimethyl ether (DIGLYME, dodochem, Suzhou, China) was used as the electrolyte. The assembly was conducted entirely in a glovebox (Vigor-LG 2400/750TS, LTD, Suzhou, China) with oxygen and water contents below 0.1 ppm.

3.8. Electrochemical Measurements

A multi-channel battery testing system (CT2001A, LAND, Wuhan, China) was used for cycling and rate performance tests. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using an electrochemical workstation (CHI 660 electrochemical workstation, Shanghai Chi-Chi Instrumentation Co., Ltd., Shanghai, China). CV scanning voltage ranged from 0.01 to 3.0 V with a scanning rate of 0.2–1.0 mV s^{−1}, while EIS frequency ranged from 0.01 to 100,000 Hz.

4. Conclusions

In summary, carbon-coated hollow Co/Ni bimetallic selenides (HS-Co_xNi_ySe@C) were obtained by sequential coating of PAN on ZIF-67, Ni²⁺ etching, and selenization. When used as anode materials for sodium-ion batteries, HS-Co_xNi_ySe@C showed improved performance and the performance of SIBs strongly dependent on the ratio of Co²⁺ to Ni²⁺, which was ascribed to enhanced surface area and conductance of Na⁺ due to the formation of the hollow structure, increased ion diffusion pathways, and the synergistic effect between Co and Ni. The excessive Ni²⁺ content caused contraction of the hollow space and condensation of the shell, which reduced the electrochemical surface area and impaired ion transport efficiency. The optimized HS-Co_xNi_ySe@C delivered a discharge capacity of 335 mAh g^{−1} after 1000 cycles at a high current density of 5.0 A g^{−1}, indicating its strong potential for commercial applications. This study not only demonstrates the superior electrochemical performance of the hollow CoNi-Se@C material but also provides innovative guidance for the design of multi-metal materials used for energy storage.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics13030096/s1>, Figure S1: Raman spectra of CoNi-Se@C; Figure S2: CV curves for the first 3 cycles of (a) CoSe₂@C, (b) CoNi-1-Se@C, and (c) CoNi-3-Se@C at 1.0 mV s^{−1}; Figure S3: XRD pattern of CoNi-Se@C after discharged to 0.01 V; Figure S4: EIS spectra and the fitted result; Figure S5: Discharge–charge curves at various rates of (a) CoSe₂@C, (b) CoNi-1-Se@C, and (c) CoNi-3-Se@C; Figure S6: TEM images of CoNi-Se@C after cycling at 5.0 A g^{−1} for 1000 cycles; Figure S7: (a,c,e) CV curves at various scan rates. (b,d,f) The corresponding log (i) versus

log (v) plots at each redox peak. Among them, (a,b) correspond to CoSe₂@C, (c, d) CoNi-1-Se@C, and (e,f) CoNi-3-Se@C; Table S1: The atomic ratio of Co, Ni, and Se in CoNi-Se@C measured by ICP-OES; Table S2: The atomic percentages of Co, Ni, Se, N, and C in CoSe₂@C, CoNi-1-Se@C, CoNi-Se@C, and CoNi-3-Se@C measured by XPS. Electrochemistry performance of different anode materials for SIBs; Table S3: The potentials (V vs Na⁺/Na) in CV scans derived from Figure 4a; Table S4: Electrochemical impedance spectroscopy equivalent circuit parameters table of CoSe₂@C, CoNi-1-Se@C, CoNi-Se@C, and CoNi-3-Se@C; Table S5: Comparison of the long cycle performance of CoNi-Se@C and metal selenides from published articles. References [24,39–46] are cited in the Supplementary Materials.

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