Selenium-based materials are considered as desirable candidates for potassium-ion and sodium-ion storage. Herein, an in situ fabrication method is developed to prepare an integrated cuprous selenide electrode by means of directly chemical selenization of the copper current collector with commercial selenium powder. Interestingly, only the electrolyte of 1 M potassium hexafluorophosphate dissolved in 1,2-dimethoxyethane with higher occupied molecular orbital energy and lower desolvation energy facilitates the formation of polyselenide intermediates and the further selenization of the copper current collector. Benefiting from the unique thin-film-like nanosheet morphology and the robust structural stability of the integrated electrode, the volume change and the loss of selenide species could be effectively restrained. Therefore, high performance is achieved in both potassium-ion batteries (462 mA h g\(^{-1}\) at 2 A g\(^{-1}\) for 300 cycles) and sodium-ion batteries (775 mA h g\(^{-1}\) at 2 A g\(^{-1}\) for 4000 cycles). The facile fabrication strategy paves a new direction for the design and preparation of high-performance electrodes.

1. Introduction

Developing high-performance energy storage devices is crucial for the effective utilization of renewable energy sources such as solar, wind, and tidal energy with the intermittent nature, securing the sufficient energy supply for sustainable development of modern society. Sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) are recognized as the competitive alternatives to lithium-ion batteries (LIBs) for the next-generation energy storage in consideration of sufficient reserves and low cost of the resources.\[1–3\] However, the development of SIBs and PIBs has been hindered by the inherent sluggish reaction kinetics of the systems and the large volume variation of electrode materials during charge and discharge processes.\[4–6\] Therefore, exploring electrode materials with high specific capacity, prominent rate capability, and superior cycling stability is of great significance to achieve high-performance SIBs and PIBs.

Selenium-based electrode materials, including selenium compounds and selenium-containing composites, have attracted considerable attention owing to their high theoretical capacity and good electronic conductivity.\[7–10\] Nevertheless, the practical application of Se-based electrode materials has still been hampered by two main issues. On the one hand, the huge volume fluctuation upon cycling gives rise to the agglomeration and the cracking of Se-based electrodes, resulting in the severe degradation in performance.\[11–13\] Extensive efforts have been made to buffer the volume change of Se-based electrodes via nanocrystallization,\[14–16\] morphology regulation,\[17–20\] and hybrid composites construction,\[21–24\] which, unfortunately, might not be satisfactory for the practical production due to their...
The facile and efficient fabrication strategy in the present work aimed to prepare the integrated cuprous selenide \((\text{Cu}_2\text{Se})\) electrode for SIBs and PIBs via the direct reaction between the commercial selenium powder and the copper current collector. Specifically, the selenium casting on the copper current collector tends to transform into soluble polyselenides spontaneously after being assembled in the battery with the ether-based electrolyte at the early stage, followed by the further reaction with the copper foil to form \(\text{Cu}_2\text{Se}\) after a relaxation period of 10 h. The comprehensive reaction mechanism was revealed via a series of external experiments combined with the theoretical calculation. The obtained \(\text{Cu}_2\text{Se}\) electrode showed a self-assembled nanosheet morphology, which is beneficial to the penetration of the electrolyte and the alleviation of the electrode volume expansion upon cycling. Moreover, the strong interaction between the selenium species and the electrode is favorable for the restriction of active materials loss. Benefiting from the improved reaction kinetics, the reduced volumetric expansion, as well as the mitigated side reactions, the in situ fabricated \(\text{Cu}_2\text{Se}\) electrode demonstrated superior sodium and potassium storage performance (high reversible capacity of 775 and 462 mA h g\(^{-1}\) at 2 A g\(^{-1}\) for SIBs and PIBs, respectively). The facile and efficient fabrication strategy in the present work provides insights into the rational design and the practical production of the high-performance selenium-based electrodes for various energy storage devices.

2. Results and Discussion

2.1. Fabrication and Characterization of the Electrode

To prepare the precursory electrode, commercial selenium powder, Super P, and carboxyl methyl cellulose (CMC) binder were dispersed in deionized water with a weight ratio of 7:2:1, and then pasted on the rough side of copper foil to improve adhesion. After being dried at 80 °C for 12 h in vacuum, the precursory electrode with a mass loading of \(\approx 1-1.5\) mg cm\(^{-2}\) was obtained. X-ray diffraction (XRD, Figure S1, Supporting Information) of the precursory electrode reveals mixed phases including Se and Cu, and the precursory electrode remained stable as confirmed by the X-ray photoelectron spectroscopy (XPS, Figure S2, Supporting Information). Then, the integrated cuprous selenide electrode was prepared by assembling the cell using the precursory electrode and the potassium foil with the electrolyte of 1 M potassium hexafluorophosphate (KPF\(_6\)) dissolved in 1,2-dimethoxymethane (DMF), as illustrated in Figure 1a. After relaxing for 10 h, \(\text{Cu}_2\text{Se}\) was dramatically formed via the gradually chemical reactions between Se and Cu foil with the impact of specific electrolyte accompanied by the complete vanish of selenium. As shown in Figure 1b, all the XRD reflections of the obtained electrode can be indexed on the basis of the cubic \(\text{Cu}_2\text{Se}\) (PDF#65-2982) with a space group of \(\text{Fm}-\text{3m}\). Furthermore, the \(\text{Se}\) 3d high-resolution XPS spectrum of the electrode (Figure 1c) exhibits two peaks centered at 53.9 and 54.8 eV, corresponding to \(\text{Se}^{2-}\) 3d\(_{5/2}\) and \(\text{Se}^{2+}\) 3d\(_{3/2}\) for \(\text{Cu}_2\text{Se}\). As for the Cu 2p spectrum (Figure 1d), two peaks centered at around 932.9 and 952.7 eV are consistent with 2p\(_{3/2}\) and 2p\(_{1/2}\) of \(\text{Cu}^{+}\), respectively.

The low magnification scanning electron microscopy (SEM) image shows that the electrode presented a cluster-like morphology assembled by the thin-film-like nanosheets (Figure 1e). Particularly, the nanosheets interwove to form a nanoporous network (Figure 2f), which can be further revealed by the transmission electron microscopy (TEM) image (Figure 1f). Such unique structure could not only effectively facilitate the electrolyte infiltration and the charge transfer, but also significantly relieve the volume variation upon cycling, ensuring the superior electrochemical performance of batteries. Energy-dispersive X-ray spectroscopy mapping (Figure S3e, Supporting Information) confirms a uniform distribution of Cu and Se elements in the electrode. Furthermore, the high-resolution TEM (HRTEM) image (Figure 1g) displays a series of lattice fringes with the spacing distance of 0.20 and 0.33 nm, corresponding to the (220) and (111) planes of \(\text{Cu}_2\text{Se}\). This result is in accordance with the XRD pattern (Figure 1b) and the XPS spectra (Figure 1c,d), demonstrating the successful chemically in situ fabrication of the integrated \(\text{Cu}_2\text{Se}\) electrode.

2.2. Evolution Processes of the Integrated Electrode

The chemically in situ fabrication progress of the integrated \(\text{Cu}_2\text{Se}\) electrode was preliminarily embodied in the voltage variation during the relaxation period. As shown in Figure 2a, the voltage of the assembled cell with precursory electrode was measured to be 2.65 V at the initial stage, which experienced a small rise and then dropped below 2.20 V during the 10-h period of relaxation. Such a voltage variation implies the evolution of phases, morphology, and interfacial properties for the electrode during the relaxation period. To gain further understanding on the formation processes of the integrated \(\text{Cu}_2\text{Se}\) electrode, the morphology variation and the phase evolution of the electrode at different relaxation stages have been comprehensively investigated. To begin with, SEM was employed to observe the morphology variation of the electrode. The bulk Se with a smooth surface in the precursory electrode (Figure 2b) tended...
to split into small pieces after the cell was relaxed for an hour (Figure 2c). With the prolongation of relaxation period, the pieces gradually converted into nanoplates with a decreasing thickness, and finally formed the interconnected ultrathin nanosheets (Figure 2d–f). Furthermore, the content of Cu in the electrode material gradually increased with the relaxation period (Figure S3, Supporting Information), while Cu and Se elements uniformly distributed in the final product when the integrated Cu$_2$Se electrode was obtained after 10 h.

Subsequently, the phase evolution was monitored via XRD and UV–vis absorption spectroscopy combined with the external experiment analysis (see Experimental Section for details). As shown in Figure S4, Supporting Information, the electrode was composed of the trigonal Se at the beginning of the reaction process. After being relaxed for an hour, several new diffraction peaks corresponding to the tetragonal Cu$_3$Se$_2$ and cubic Cu$_2$Se emerged in the XRD pattern of the electrode except for the peaks from the original Se (Figure S4, Supporting Information). Aiming to give an insight into the reaction processes, the electrode that relaxed for 1 h was fetched out from the cell and then immersed in DME. The color of the solution turned dark brown after adding the electrode (inset of Figure 2g), probably due to the formation of soluble potassium polyselenide intermediates during the first hour relaxation. Then, the solution was detected via UV–vis absorption spectroscopy measurement to identify the specific ingredients. A broad peak emerged at around 587 nm indeed demonstrated the formation of soluble polyselenides (Figure 2g), which could easily react with Cu to form copper selenides.$^{[35]}$ The reduction of selenium and the selenization of Cu foil continuously proceeded after the cell being relaxed for 2 h, maintaining the coexistence of Se, Cu$_2$Se, and Cu$_3$Se$_2$ (Figure 2g and Figure S4, Supporting Information). After a 5-h relaxation, it seems that most of the polyselenides re-acted with the Cu foil as the DME solution soaking the electrode is almost colorless (inset of Figure 2g). However, the UV–vis spectrum and the XRD pattern are suggestive of an incomplete reaction on the electrode (Figure 2g and Figure S4, Supporting Information), though the cuprous selenide was the major ingredient of the electrode. Eventually, the reaction went to completion after the cell was relaxed for 10 h, all the Se reacted with the Cu foil to form cuprous selenide (Figure S4, Supporting Information).
Additionally, the electrodes with different relaxation periods exhibited diverse electrochemical properties according to their galvanostatic charge/discharge (GCD) profiles and the corresponding differential capacity versus voltage (dQ/dV) curves, which provided further evidence for the phase evolution from another perspective (Figure S5, Supporting Information). As shown in Figure S5a–c, Supporting Information, the fresh battery with no relaxation period exhibited a redox pair at around 2.2 V in the first cycle, which could be assigned to the potassiation and depotassiation processes of selenium. The intensity of these redox peaks significantly reduced accompanied by the appearance of new redox pairs for the battery with a relaxation period of 1 h (Figure S5d–f, Supporting Information), indicating the phase transition of the precursory electrode so as to change the charge and discharge behavior of the battery. With the extension of relaxation period, the new redox pairs were intensified, and the capacity of the battery was increased simultaneously. In contrast, the redox for the (de)potassiation of selenium dwindled, corresponding to the continuous consumption of the pristine Se. Finally, the redox potential for the electrode with a relaxation period of 10 h accorded exactly with that of the (de)potassiation for cuprous selenide (Figures S5m–o and S6, Supporting Information), illustrating the successful fabrication of the integrated cuprous selenide electrode. Notably, both the capacity and the redox intensity increased with the prolonging relaxation period of the batteries in the second cycle, demonstrating the better reversibility of the integrated cuprous selenide electrode. Based on the above analysis, the evolution process of the electrode can be summarized as shown in Figure 2h. After being assembled in the battery, the bulk selenium on the electrode gradually transforms into soluble polyselenides. Then, the polyselenides infiltrate from the crack of selenide, and react with the copper current collector to form a series of selenides such as Cu₂Se₂ and Cu₃Se. As the reaction progress, the integrated Cu₃Se electrode with nanosheet-like morphology can be obtained on account of the reducibility of selenium species.

### 2.3. Key Factors for the Selenization of the Cu Current Collector

Notably, since the assembled battery was at an open circuit state during the relaxation period, the generation of intermediate polyselenides and the selenization of the copper current collector originated from the chemical reactions on the surface of the electrode rather than the electrochemical reactions, and related to the specific electrolyte (1 m KPF₆ dissolved in DME). When the electrolyte solvent was replaced with ethylene carbonate (EC)/propylene carbonate (PC) with a volume ratio of 1:1, the
GCD profiles of the battery (Figure 3a) were totally different from those of the battery using 1 m KPF₆ dissolved in DME after a 10-h relaxation (Figure 3b). The only plateau presented during the discharge process derives from the single phase-change reaction of Se in the carbonate-based electrolytes. While the lower capacity and the charging irreversibility originate from the large particle size of the commercial Se chain, the high reaction barrier of the one-step solid reaction, as well as the side reaction between the discharge product KₓSe and the carbonate-based electrolyte. The XRD pattern also corroborates that the selenium in the precursory electrode remained unchanged after being relaxed in 1 m KPF₆ in EC/PC for 10 h (Figure S7, Supporting Information). Therefore, the employment of carbonate-based electrolyte could not induce the in situ fabrication of the integrated Cu₂Se electrode, even if using KPF₆ as the salt. Besides, the salt of the electrolyte also makes a considerable impact on the entire system. For comparison, the electrolyte was prepared by substituting potassium bis(fluorosulfonyl)imide (KFSI) for KPF₆ in DME solvent. As shown in Figure S7, Supporting Information, the electrode maintained the original selenium phase after being relaxed in the electrolyte of 1 m KFSI in DME for 10 h. In addition, the initial charge and discharge behavior of the battery with 1 m KFSI in DME as the electrolyte was in agreement with the two-phase transition process of Se electrode in ether-based electrolyte (Figure 3c), and significantly deteriorated upon cycling due to the sluggish kinetics of Se electrode and the continuous loss of the Se species in ether-based electrolyte. In consequence, the integrated Cu₂Se electrode could only be in situ fabricated using specific electrolyte (1 m KPF₆ in DME) so as to achieve superior electrochemical performance.

In order to gain a better understanding of the electrolyte selectivity to fabricate the integrated Cu₂Se electrode, an interfacial model based on one potassium ion coordination structure was introduced to illustrate the in situ selenization process of the current collector via density functional theory (DFT) calculations. Generally, the solvated structure with a lowest energy is the main species in the electrolyte. Specifically, the cations coordinate with the solvent molecules in the first solvation shell, and the anions stay around the solvation shell with a certain distance from the cations in the diluted electrolyte (e.g., a concentration of around 1 m). The optimized geometrical structures of salt–solvent complexes for the above-mentioned three different electrolytes are presented in Figure 3d. The highest occupied molecular orbital (HOMO) of KPF₆-EC/PC is much lower than those of KFSI-2DME, KPF₆-2DME and even Se₁₃ cluster, so the reduction of bulk selenium to polyselenide would hardly occur in the carbonate-based electrolyte. As for the ether-based electrolyte systems, although the KFSI-2DME system possesses a higher HOMO energy, which is preferable for the generation of polyselenide (Figure S9, Supporting Information), its higher desolvation energy (Figure 3e) probably renders a robust interaction between the polyselenide species and the solvated structure, which prevents the further
selenization of Cu foil. These results interpret why the in situ fabrication of the integrated Cu₂Se electrode could only take place in the specific electrolyte system (1 M KPF₆ in DME). Besides, it is worth noting that, owing to such an anion-induce effect, the soluble selenium species generated during the electrochemical process in KFSI/DME electrolyte would not react with Cu current collector, causing the fast capacity degradation as shown in Figure 3c. In addition, the cation of the electrolyte salt could impact the selenization process. When assembled the precursor electrode in a SIB with an electrolyte of 1 M sodium hexafluorophosphate (NaPF₆) in DME, the coexistence of Se, intermediate Cu₅Se₂, and Cu₂Se was observed even after a relaxation time of 10 h (Figure S10, Supporting Information). It demonstrates a slower evolution kinetics of the electrode in SIB compared with that in PIB, probably due to the stronger interaction between the solvent molecular and sodium ions, which possess higher Lewis acidity than potassium ions.[42] Accordingly, the in situ fabrication of the integrated Cu₂Se electrode might be achieved in other battery systems via electrolyte regulation, paving a new way for the design and the preparation of the electrode.

Except for the electrolyte, the mass loading would also affect the fabrication process of the integrated Cu₂Se electrode. The precursory electrodes with different mass loading (≈0.5–0.75 and ≈2.0–3.0 mg cm⁻²) were produced for comparison. In the case of electrode with lower mass loading, the selenization of Cu current collector was faster with a shorter existing time of the intermediate Cu₅Se₂ (Figure S11, Supporting Information). It is ascribed with the shorter diffusion path of the polyselenides on the precursory electrode with lower mass loading, corresponding to an easy access of copper. By contrast, the precursor electrode with higher mass loading exhibited an incomplete conversion even after a 10-h relaxation. Particularly, the diffraction peaks of Cu₅Se₂ remained after 10 h as shown in Figure S12, Supporting Information, indicating the slower diffusion kinetics of the polyselenides toward copper current collector due to the higher mass loading. Therefore, a proper mass loading of the precursory electrode is of significance for the complete selenization of the copper current collector.

Furthermore, the copper current collector with high affinity toward Se is another key factor to fabricate the integrated Se-based electrode. For comparison, aluminum (Al), nickel (Ni), and titanium (Ti) foils were also employed as the current collector, and the corresponding precursory electrodes were prepared in the same way (seen details in Experimental Section). After a 10-h relaxation, the electrodes with different current collectors were also fetched out from the batteries using 1 M KPF₆ in DME as the electrolyte, and then immersed in DME solvent. The DME solvent displayed a color of brown for all three control groups (Figure S13, Supporting Information). The XRD patterns also demonstrate that Se completely maintains its original phase without any changes for the electrodes with Al, Ni, and Ti as the current collector (Figure S14a–c, Supporting Information). The GCD profiles (Figure S14d–f, Supporting Information) of the batteries using these three current collectors are consistent with the intrinsic galvanostatic charge and discharge curves of Se, which has been illustrated in Figure S5a, Supporting Information. Thus, the copper current collector with unique selenophilic nature is indispensable for the in situ fabrication of integrated electrode.

2.4. Potassium Ions Storage Behavior

According to Figure 3b, the integrated Cu₂Se electrode delivered a high specific capacity of 548 mA h g⁻¹ with superior cyclic reversibility. The GCD profiles with several plateaus and inflections demonstrate a multi-step potassiation/de-potassiation process, which can be observed more clearly through the cyclic voltammetry (CV) test (Figure 4a). In the first cycle, two obvious peaks appearing at 0.94 and 0.57 V in the cathodic scan can be assigned to the insertion of potassium ions into the lattice of Cu₂Se followed by the conversion reaction to form copper and potassium selenides. In addition, a small cathodic peak at 0.11 V, which disappeared after the first scan, can be attributed to the formation of solid electrolyte interface (SEI) film. Upon the initial anodic process, a series of redox peaks emerged in the voltage range from 1.3 to 2.6 V, representing the multiple depotassiation stages including conversion reaction (1.79 V) and extration reaction (2.07 and 2.57 V). Notably, the cathodic/anodic curves for the subsequent scans are almost coincident, displaying a good reversibility and stability during repeatable potassiation and depotassiation. The slight shift of the redox peaks in comparison with the first scan is attributed to some irreversible structure changes, such as the microstructure and the surface/interface properties of the materials, which may facilitate the reversible electrochemical reaction and ensure the fast redox kinetics in subsequent cycles.[13,44]

Figure 4b shows the cyclic performance of the integrated Cu₂Se electrode at a current density of 0.5 A g⁻¹. The discharge capacity of the battery was 661 mA h g⁻¹ (based on the active material of Se) for the first cycle, and remained almost unchanged after 50 cycles with a highly capacity retention of 98.8%. The Coulombic efficiency for the initial cycle was ≈88.7%, which is slightly lower due to the irreversible reactions, and increased above 99.8% after the second cycle. The XRD pattern of the integrated Cu₂Se electrode after being cycled demonstrates the superior reversibility of the Cu₂Se electrode (Figure S15, Supporting Information), corresponding to the high Coulombic efficiency upon cycling. Subsequently, the electrochemical impedance spectroscopy spectra (EIS) of the integrated Cu₂Se electrode were collected after various cycles to estimate the electrode evolution upon cycling. As shown in Figure 4c, all the Nyquist plots consist of a single semicircle with an oblique line. The depressed semicircle is related to the charge-transfer resistance (Rₜ) at the interface between the electrolyte and the electrode, while the oblique line is interpreted as the Warburg resistance reflecting the potassium diffusion in the bulk electrode.[45] As shown in Table S1, Supporting Information, the Rₜ value for the first cycle is slightly higher than that at the open-circuit voltage (OCV) state, which correlates to the formation of SEI film. After 10 cycles, the Rₜ increased due to the activation process of the electrode materials, and basically remained on the same order of magnitude after 50 cycles, ensuring the fast kinetic of the battery to achieve stable cycling performance. Furthermore, the long-term cycling stability of the integrated Cu₂Se electrode was estimated at a current density of 2 A g⁻¹ (Figure 4d). A reversible capacity of 462 mA h g⁻¹ was achieved over 300 cycles with a stable Coulombic efficiency of nearly 100%. The impressive cyclic performance might arise from the unique interconnected ultrathin nanosheet morphology of the integrated Cu₂Se electrode, which could not only
effectively facile reaction kinetics, but also relieve the volume variation of the conversion-type materials. While the ex situ SEM images confirm the morphology integrity of electrode with a nanoporous network after cycling (Figure S16, Supporting Information). Except for the interconnected ultrathin nanosheet morphology, the robust adhesive force of the active materials on the current collector, which is attributed to the in situ chemical fabrication process rather than the binder adhesion, is also beneficial for the prolonged cycle life of the battery. Benefiting from the rational design of the integrated electrode structure, the integrated Cu$_2$Se electrode also exhibited superior rate capability. As shown in Figure 4e, the integrated Cu$_2$Se electrode displayed high reversible capacities of 647, 598, 588, and 541 mA h g$^{-1}$ at 0.2, 0.5, 1, and 2 A g$^{-1}$, respectively. Even at a high rate of 2 A g$^{-1}$, it still delivered an 84% capacity retention with respect to 0.2 A g$^{-1}$. Besides, the reversible capacity recovered to 644 mA h g$^{-1}$ as the current density returned to 0.2 A g$^{-1}$, indicating excellent structure stability of the integrated Cu$_2$Se electrode.

2.5. Sodium Ions Storage Behaviors

To extend the utilization of the integrated Cu$_2$Se electrode, the sodium-ion storage performance of the in situ fabricated electrode was comprehensively investigated using a corresponding ether-based electrolyte of 1 M NaPF$_6$ in DME. The detailed assembling process of the SIB is provided in the Experimental Section. The electrochemical process of the integrated Cu$_2$Se electrode in SIBs is analogous with that in PIBs, including the insertion/extraction and conversion reactions as shown in CV curves (Figure 5a). In the initial cathodic scan, the peak emerged at 1.62 V, which intensified in the subsequent scans, with some small humps between 1.7 and 1.0 V represents the insertion of sodium ions in the Cu$_2$Se. The obvious peak at 0.67 V belongs to the conversion reaction to form metal Cu and Na$_2$Se. The increasing intensity of cathodic peaks in the subsequent scans originated from the activation of the electrode after a reversible Na$^+$ intercalation-deintercalation process during the initial scan. In the initial anodic scan, two oxidation peaks around 1.53 and 2.01 V are attributed to the desodiation process generating the Cu$_2$Se structure with lattice vacancy. The structure evolution with the formation of lattice vacancy might be responsible for the peak shifting in the subsequent scans. Figure 5b presents the GCD profiles of the integrated electrode, which is in accordance with the CV curves. Benefiting from the unique morphology and the microstructure, the Cu$_2$Se electrode delivered a highly reversible specific capacity of 743 mA h g$^{-1}$ (Figure 5c), which retained to be 727 mA h g$^{-1}$ after 50 cycles with a corresponding retention of 98%. The excellent cycling stability is due to the high reversibility of the integrated Cu$_2$Se electrode (Figure S17, Supporting Information). To gain insight into the origin of the fascinating electrochemical performance, EIS was conducted after various cycles as shown in Figure 5d. The impedance of the battery did not increase significantly after 50 cycles (Table S2, Supporting Information), revealing the great stability of the electrode structure so as to achieve superior cycling performance. Additionally, the fast kinetics is favorable for the rate performance of the integrated Cu$_2$Se electrode (Figure 5e). As the current density increased from 0.2 to 5 A g$^{-1}$, the specific capacity of the battery was preserved to be 755 mA h g$^{-1}$, only 2.1% decrease compared with the capacity at 0.2 A g$^{-1}$. Moreover, the GCD profiles of the integrated Cu$_2$Se electrode at various current densities effectively facilitate the insertion of sodium ions into the electrode.
overlap well without significant increase of overpotential (Figure 5f). Such an unprecedented rate performance is not only because of the unique structure of the integrated electrode which could facilitate the fast charge transfer during electrochemical process, but also due to the enhancement of conductivity derived from the structure vacancy and sodium-ion insertion.\textsuperscript{[46,47]} Encouraged by this fast sodium ion storage performance, the long-term cycling capability of the integrated Cu\textsubscript{2}Se electrode was estimated at a high rate of 2 A g\textsuperscript{-1} as shown in Figure 5g. During the cycling process, the specific capacity of the integrated Cu\textsubscript{2}Se electrode remained stable even with no significant fluctuation, demonstrating a $\approx$100\% capacity retention after 4000 cycles. The prominent electrochemical performance is ascribed to the rational design of the integrated Cu\textsubscript{2}Se electrode with the interconnected ultrathin nanosheets morphology and the robots interaction between the active materials and the current collector. Different from the negative effect of the reaction between the current collector and the active materials in the conventional battery systems, the in situ selenization of the copper current collector in this work emerges as a facile and effective approach to fabricate an integrated Cu\textsubscript{2}Se electrode with enhanced electrochemical performance. On one hand, the in situ chemical fabrication strategy partially converts the copper current collector, that is inert in other battery systems, into a component of active materials. It is equivalent to increasing the ratio of active material in the electrode while keeping the total mass of the electrode constant, which is of considerable importance to achieve a high energy density of the battery. On the other hand, the unique structure endows the electrode with the capabilities to facilitate the mass transition, buffer the volume change, and prevent the loss of active materials. Thus, the in situ fabricated Cu\textsubscript{2}Se electrode displays exceptional performance for potassium- and sodium-ion storage, and possesses the potential for practical application.

3. Conclusion

In summary, a facile in situ fabrication method is proposed to prepare an integrated Cu\textsubscript{2}Se electrode through the directly...
chemical seleniumization of the copper current collector with commercial selenium powder. During the in situ seleniumization process, the composition of electrolyte plays a key role in the formation of polyseelenide intermediates and the further seleniumization of the copper current collector. The as-obtained integrated CuSe electrode with interconnected nanosheet morphology is not only favorable to facilitate the transmission of electrolyte and charge carriers, but also beneficial to alleviate the volume expansion during the conversion reaction. As a result, the integrated CuSe electrode exhibits superior sodium-ion (775 mA h g⁻¹ at 2 A g⁻¹ for 4000 cycles) and potassium-ion storage performance (462 mA h g⁻¹ at 2 A g⁻¹ for 300 cycles). The facile in situ fabrication strategy provides guidance for the design and preparation of high-performance electrodes for practical application.

4. Experimental Section

Chemicals and Materials: All the chemicals were of analytical grade and directly used. Selenium powder, CM, DME were all purchased from Sigma Aldrich. Cuprous selenide was purchased from Aladdin Reagent.

Fabrication of Electrodes: Commercial Se powder (or cuprous selenide), Super P conductive additive, and CMC binder with a weight ratio of 7:2:1 were dissolved in deionized water to prepare the slurry casting on the current collectors (Cu, Ni, Ti, and Al foil). After being dried in a vacuum oven at 80 °C for 12 h, the as-prepared electrodes were punched into discs with the diameter of 10 mm. The mass loading of the active material was measured to be ≈1–1.5 mg cm⁻².

External Experiments: The electrodes that relaxed for 0, 1, 2, 5, 10 h were fetched out from the batteries and then immersed in DME solvent, which has usually been employed as the solvent to dissolve polyseelenides.

Materials Characterization: The crystal structure of the sample was studied by XRD measurement on a Bruker D8 Advance Diffractometer with Cu Kα radiation. The morphologies and the microstructures of the samples were investigated using a NOVA 230 field-emission scanning electron microscopy and a FEI Titan 80–300 HRTEM. X-ray photoelectron spectra were tested by using a VG scientific ESCALAB-250 spectrometer. UV–vis absorption spectra were conducted on a Shimadzu UV-1900 spectrophotometer.

Electrochemical Measurement: The electrochemical properties of the electrodes were evaluated by assembling 2032-type coin cells in the argon filled glovebox. Potassium and sodium foils served as the counter electrodes for PIBs and SIBs, respectively. Glass fiber filter (Whatman GF/F) and direct used. Seleniumpowder, CMC,DME were all purchased from SigmaAldrich.Cuprous selenide was purchased from AladdinReagent. 

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

cuprous selenides, electrode materials, potassium-ion battery, sodium-ion battery
