Enabling fast-charging selenium-based aqueous batteries via conversion reaction with copper ions

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Selenium (Se) is an appealing alternative cathode material for secondary battery systems that recently attracted research interests in the electrochemical energy storage field due to its high theoretical specific capacity and good electronic conductivity. However, despite the relevant capacity contents reported in the literature, Se-based cathodes generally show poor rate capability behavior. To circumvent this issue, we propose a series of selenium@carbon (Se@C) composite positive electrode active materials capable of delivering a four-electron redox reaction when placed in contact with an aqueous copper-ion electrolyte solution (i.e., 0.5 M CuSO₄) and copper or zinc foils as negative electrodes. The lab-scale Zn | Se@C cell delivers a discharge voltage of about 1.2 V at 0.5 A g⁻¹ and an initial discharge capacity of 1263 mAh g⁻¹. Interestingly, when a specific charging current of 6 A g⁻¹ is applied, the Zn | Se@C cell delivers a stable discharge capacity of around 900 mAh g⁻¹ independently from the discharge rate. Via physicochemical characterizations and first-principle calculations, we demonstrate that battery performance is strongly associated with the reversible structural changes occurring at the Se-based cathode.

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Lithium-sulfur (Li–S) batteries have been considered as one of the most promising energy storage systems as sulfur cathodes show merits of high theoretical specific capacity and low cost. However, sulfur suffers from its low intrinsic electronic conductivity, which leads to low active material utilization and unsatisfactory rate performance. In addition, the low density of sulfur also prevents it from achieving high areal/volumetric electrochemical performance in real devices. Selenium (Se) is a chalcogen element that also shows many advantages in electrochemistry non-standard and standard states. Using a Se@C composite with 48 wt.% of Se, the Zn | Se@C full cell shows an initial discharging capacity of 1263 mAh g$_{\text{Se}}$ at 0.5 A g$^{-1}$ with a stable discharging plateau at ~1.2 V and can be efficiently charge/discharge for 400 cycles at 2 A g$^{-1}$.

Results

Synthesis and characterizations of the Se@C composite. A honeycomb-like porous carbon was used as the Se host, and the Se@C composite was obtained after a melt-diffusion treatment (Supplementary Fig. 1). As shown in Fig. 1a, the X-ray diffraction (XRD) pattern of Se@C composite is matched with crystalline Se (JCPDS: 06-0362). The Raman spectrum shows two intense peaks at 138.8 and 236.9 cm$^{-1}$, which are assigned to Se (Fig. 1b). The specific surface area of the Se@C composite is 173 m$^2$ g$^{-1}$, which is lower than that of bare carbon host (370 m$^2$ g$^{-1}$, Fig. 1c). Thermogravimetric analysis (TGA) shows the Se content in Se@C is about 48% in mass (denoted as Se@C-48, where the number represents the Se content, Supplementary Fig. 2), which is comparable to other Se-based batteries reported in the literature. Field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images show the Se@C-48 composite still maintained the honeycomb-like structure and no large Se particles (diameter <100 nm) are detected (Fig. 1d–i), suggesting a uniform distribution of Se in the porous carbon host. The element mappings also demonstrate this point (Fig. 1g–i).

Electrochemical performance of Cu | 0.5 M CuSO$_4$ | Se@C coin cells. The electrochemical performance of the Se cathode chemistry was studied in the coin cell, with Se@C-48 on carbon cloth as the cathode, a 0.5 M CuSO$_4$ solution as the electrolyte, and a Cu foil as the anode, respectively. The CV curves of Cu|0.5 M CuSO$_4$|Se@C-48 cells show three pairs of redox peaks (Supplementary Fig. 3). The cells using stainless steel as the cathode current collectors show similar cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) curves with that using carbon cloth (Supplementary Fig. 4). Considering its flexibility, carbon cloth was adopted as the cathode current collectors in the subsequent electrochemical tests.

Figure 2a shows the GCD curves of the Cu|0.5 M CuSO$_4$|Se@C-48 cells at 0.5 A g$^{-1}$. It shows a discharging plateau at about 0.16 V vs. Cu$^{2+}$/Cu (~0.50 V vs. SHE), which is more than 1.5 V higher than non-aqueous organic-based alkali metal | Se batteries (Supplementary Fig. 5 and Supplementary Table 1). The first discharge specific capacity is as high as 1298 mAh g$_{\text{Se}}$ at 0.5 A g$^{-1}$, which is close to twice of the conventional Se-based batteries. In addition, the discharge plateau is very stable, releasing about 90% of its full capacity with a charge/discharge voltage hysteresis of about 0.1 V (Fig. 2b). The voltage plateau slope, about 0.11 V/1000 mAh g$^{-1}$, is smaller than conventional Se cells, means a more stable discharging plateau (Supplementary Fig. 6a). Besides, the hysteresis between discharge and charge curve is also smaller than other Se-based cells (Supplementary Fig. 6b). Suggesting reversible reaction kinetics. The Cu|0.5 M CuSO$_4$|Se@C-48 cell delivers 1070, 1025, 939, 839, 796 mAh g$_{\text{Se}}$ at 0.5, 2, 5, 8, and 10 A g$^{-1}$, respectively (Figs. 2c, d). The discharge capacity at 10 A g$^{-1}$ is still larger than the theoretical capacity (675 mAh g$^{-1}$) of other Se-based cathodes based on a two-electrode transfer reaction. It also shows good cycling stability. A capacity retention...
**Fig. 1** Physicochemical characterizations of the Se@C-48 composite. **a** XRD pattern, **b** Raman spectrum, and **c** N₂ adsorption-desorption isotherm of Se@C-48 composite. The **d** FESEM, **e, f** TEM images, and **g-i** corresponding element mappings of the Se@C-48 composite.

**Fig. 2** Electrochemical characterization of the Cu||0.5 M CuSO₄||Se@C-48 coin cells. **a** GCD curves of the first three cycles of Cu||Se@C-48 cell (the number represents the Se content) at 0.5 A g⁻¹. **b** The discharging plateau and polarization between discharging and charging curves of Cu||Se@C-48 cell at 1 A g⁻¹. **c** Rate performance, **d** corresponding GCD curves, **e** cycling stability test (5 A g⁻¹), and **f** GCD curves at different cycles of the Cu||Se@C-48 cell.
of about 95% is achieved after 300 cycles at 5 A g\(^{-1}\), corresponding to a low decay rate of 0.017% per cycle (Fig. 2e). The GCD curves of different cycles maintain almost the same shape, further demonstrating the good stability (Fig. 2f). The Coulombic efficiency during cycling stability test is >98% except the initial three cycles (~96%). The long-term cycling performance is a result from the fact that no soluble intermediates form during the discharging/charging process, thus hindering the polyselenides from the structure of cathode during a whole discharging-charging cycle. Figure 4a, b show full patterns of in situ XRD between 10 and 55°. There are three peaks that remain constant throughout the process, which come from the XRD equipment (21.6°) and current collect (43.8° and 50.8°). Before discharging, the XRD pattern of cathode is well matched with crystalline Se (JCPDS: 06-0362) and shows a strongest peak at about 29.7°. The peaks between 25.5 and 30.5° are carefully scrutinized. As shown in Fig. 4c, d, along with the discharging, the peak of Se at 29.7° weakened and disappeared gradually. A peak at about 27.9° associated with the (112) plane of CuSe emerged, suggesting the formation of CuSe by the reduction of about 3 Ω (Supplementary Fig. 20 and Supplementary Table 2). Moreover, the fast-charging rate capability performance tests are well-positioned (especially at specific currents >5 A g\(^{-1}\)) in terms of specific discharge capacity when compared to other Se-based battery chemistry reported in the literature (Supplementary Fig. 21). In order to understand the fast-charging performance, galvanostatic intermittent titration technique (GITT) test is carried out for Cu||Se@C-78 cell. Typical gaps between each polarization potential and each quasi-equilibrium potential are as small as 15.5 and 18.9 mV for the discharging and charging processes, respectively (Supplementary Fig. 22), suggesting the fast reaction kinetics. The calculated diffusion coefficients of Cu\(^{2+}\) are in the ranges of 10\(^{-11}\) to 10\(^{-8}\) and 10\(^{-12}\) to 10\(^{-8}\) cm\(^2\) s\(^{-1}\) for discharging and charging processes, respectively (Fig. 3d, e). The electrochemical performance of Se@C-78 with higher areal loading of about 4, 8, and 12 mg cm\(^{-2}\) were also studied (Supplementary Figs. 23–25), where the highest areal capacity of 5.68 mAh cm\(^{-2}\) was achieved at an areal loading of 8 mg cm\(^{-2}\). Further increasing the areal loading to 12 mg cm\(^{-2}\) led to a decrease of the areal capacity to 4.77 mAh cm\(^{-2}\) (Supplementary Fig. 26), presumably due to the impeded mass transfer within the thick electrode that detrimentally affect the electrochemical energy storage performance.

**Working mechanism of the Cu||Se@C coin cells.** In order to study the working mechanism of the Se@C-based electrodes, in situ XRD measurements were performed to examine the Se cathode during a whole discharging-charging cycle. Figure 4a, b show full patterns of in situ XRD between 10 and 55°. There are three peaks that remain constant throughout the process, which come from the XRD equipment (21.6°) and current collect (43.8° and 50.8°). Before discharging, the XRD pattern of cathode is well matched with crystalline Se (JCPDS: 06-0362) and shows a strongest peak at about 29.7°. The peaks between 25.5 and 30.5° are carefully scrutinized. As shown in Fig. 4c, d, along with the discharging, the peak of Se at 29.7° weakened and disappeared gradually. A peak at about 27.9° associated with the (112) plane of CuSe emerged, suggesting the formation of CuSe by the reduction...
of Se. Subsequently, peaks at about 27.8°, 26.7°, and 26.3° sequentially appeared. These peaks are attributed to the (200) plane of Cu$_3$Se$_2$, (111) plane of Cu$_2$Se, and (222) of plane Cu$_2$Se, respectively, indicating further multi-step conversion reaction of the Se cathode. At the end of discharging, only the peak of Cu$_2$Se remained, proving that Se was finally converted to Cu$_2$Se in a four-electron reaction ($\text{Se} + 2 \text{Cu}^{2+} + 4 e^- \rightarrow \text{Cu}_2\text{Se}$). During the charging process, the peak of Cu$_2$Se at $\theta$ of 26.3° vanished, and the peaks of Cu$_{2-x}$Se, Cu$_2$Se$_2$, and CuSe reoccurred in order. Se was also observed in the ex-situ TEM measurements of the Se@C-48 electrode at the fully charged state (Supplementary Fig. 27), suggesting the good reversibility of the cathode reaction during the discharging/charging process. The lack of Se diffraction peaks is presumably due to its low crystallinity formed at the charging state, as also reported in the literature\textsuperscript{13,20}. The CuSe almost exists in the whole charging process, which is quite important for fast charging \textit{(vide infra)}. The discharging-charging processes of the second and third cycle were also studied by in situ XRD (Supplementary Fig. 28), demonstrating good reversibility of the four-electron Se chemistry. The ex-situ XRD was also performed, and the peaks of discharging products were matched with CuSe, Cu$_3$Se$_2$, Cu$_{2-x}$Se, and Cu$_2$Se (Supplementary Fig. 29). In a word, XRD shows the Se cathode, first-principle calculations were performed to elucidate the conversion process of Se and the origin of fast-charging/charging.}

![Fig. 4 The working mechanism of the Cu|0.5 M CuSO$_4$|Se@C-78 coin cells. a and b Full patterns of in situ XRD between 10 and 55° during a whole discharging-charging process. c and d In situ XRD patterns between 25.5 and 30.5° to show the sequential conversion of Se to CuSe, Cu$_3$Se$_2$, Cu$_{2-x}$Se, and Cu$_2$Se during the discharging process. e Schematic illustration of structure transition of Se during the discharging process.](image)
The low-resolution TEM images, corresponding element mapping images, and atomic ratio high-resolution TEM images and corresponding Fast Fourier transform (FFT) patterns of Cu₃Se₂, Cu₂Se, and Cu₂₋ₓSe. Error bars represent the standard deviation of different experiments. The atomic ratio of Cu₃Se₂, Cu₂₋ₓSe, Cu₂Se, and Cu₂Se is summarized in Fig. 5b. Here, the relative total energy is defined as:

\[ E_{rel}(\epsilon) = E_i(\epsilon) - E_{Se}(\epsilon). \]

where \( E_{rel} \) and \( E_i \) represent the total energy for Cu₃Se₂, Cu₂₋ₓSe, Cu₂Se, and Cu₂Se alloys, respectively. The relative total energy \( E_{rel} \) of Cu/Se alloys increases by ~0.1 eV, which could further promote phase transition at macroscale. Simultaneously, the rising total energy \( E_{rel} \) (around 0.5 eV) helps overcome the energy barriers between different phases; therefore the volumetric expansion due to the intercalation of copper ions during the discharging process may accelerate phase transition process as well as in this aspect. A related issue is the influence of volumetric shrinking to the phase transition during the charging process. The situation here is exactly opposite to the discharging process, as copper ions are pulled out by the electric energy, all Cu/Se alloys tend to shrink with the leaving of copper ions. For all discharging products, the total energy, \( E_{rel} \), increases and the corresponding \( E_{rel} \) decreases or even changes to a positive the sign under high volumetric shrinking (Fig. 6b), which could help speed up the conversion of Cu/Se alloys with high copper content to those with low copper content.

Additionally, the fast diffusion of copper ions is also essential to complement phase transition for rapid charging/discharging. As shown in Fig. 6c, d, Se atoms form spiral chains along the...
same direction, and it is thus assumed that the diffusion path of copper ions is along the chain axis due to the quasi-one-dimensional structure. To assess the diffusion energy barrier, the initial positions of six copper ions between two nearest neighboring Se atoms are set with equal distance from each other and structural relaxation is applied to calculate the total energy. It should be noted that during relaxation, copper ions can only move in the plane perpendicular to the chain axis. The obtained energy variation suggests a high diffusion energy barrier of ~0.54 eV at zero strain, which is difficult to trigger a fast diffusion. However, such a barrier considerably decreases under tensile strain (0.06 eV and 0.17 eV at 5% and 10% strain, respectively, Fig. 6e), suggesting the volumetric expansion contributes to fast copper ions diffusion in Se lattice. Further-more, the diffusion of copper ions in CuSe is examined in details. As CuSe dominates the entire charging process according to XRD results (Fig. 4c, d), the fast charging should be closely related to the diffusion of copper ions in CuSe. Meanwhile, with the discharging rate primarily limited by the diffusion of copper ions through low-Cu-content domains, CuSe is the ideal model since it has the lowest copper content in all discharging products. The model of CuSe with one copper-ion embedded is shown in Fig. 6f, g, where the diffusion process is marked by red arrows and two copper ions work collectively to render an effective diffusion process marked by the blue arrow. The energy evolution during this interstitial and vacancy pair mediated diffusion process is shown in Fig. 6h, and a relative low diffusion energy barrier of 0.174 eV is predicted, which accounts for the fast charging/discharging rates observed in the experiments. Moreover, the electrical conductivities of pure copper and all copper selenium compounds (CuSe, Cu3Se2, Cu2−xSe, Cu2Se) are calculated by first-principle method. All intermediates (CuSe, Cu3Se2, Cu2−xSe) have decent conductivities (about one-tenth of pure copper) that could contribute to fast charging (Supplementary Fig. 44).

To demonstrate the use of the Se@C-based electrodes in other electrochemical energy storage systems, an aqueous home-made Zn | Se@C-48 full cell is assembled using an electrolyte solution comprising of 0.5 M CuSO4 and 0.5 M ZnSO4 (Fig. 7a). Supplementary Fig. 45 shows its photographic picture. An anion-exchange membrane is used to prevent the direct contact of the Cu2+ ions with the Zn metal. The SO42− anions of the electrolyte serve as charge balance and are able to move through...
During the discharging process, the Se cathode gets electrons and reacts with Cu\(^{2+}\) ion to be converted to Cu\(_2\)Se. Concomitantly, the zinc anode loses electrons and then gets oxidized to Zn\(^{2+}\). The reactions during the discharging process are as following:

**Cathode**

\[
\text{Se} + 2\text{Cu}^{2+} + 4e^- \rightarrow \text{Cu}_2\text{Se}
\]

**Anode**

\[
2\text{Zn} - 4e^- \rightarrow 2\text{Zn}^{2+}
\]

**Full cell**

\[
\text{Se} + 2\text{Cu}^{2+} + 2\text{Zn} \rightarrow \text{Cu}_2\text{Se} + 2\text{Zn}^{2+}
\]

Benefiting from the low redox potential of Zn (−0.76 V vs. SHE\(^{35–37}\)), the aqueous Zn||Se@C-48 full cell delivers a stable discharging voltage of about 1.2 V at 0.5 A g\(^{-1}\). The initial discharging capacity is up to 1263 mAh g\(_{\text{Se}}\)^\(-1\), corresponding to a specific energy of 1500 mWh g\(_{\text{Se}}\)^\(-1\) (Fig. 7b). It delivers a reversible discharging capacity of about 1000 mAh g\(_{\text{Se}}\)^\(-1\) in the subsequent cycles. Meanwhile, it also shows a charge/discharge hysteresis of about 0.2 V and an energy efficiency of 85.7% at 0.5 A g\(^{-1}\). The aqueous Zn||Se@C-48 full cell could stably work for 400 cycles without significant capacity degradation at 2 A g\(^{-1}\) (Fig. 7c). The Coulombic efficiency during cycling stability test is >98%. It could store about 900 mAh g\(_{\text{Se}}\)^\(-1\) in 9 min (charging at 6 A g\(^{-1}\), Fig. 7d, e), demonstrating the great potential in fast-charging applications.

**Discussion**

In summary, we have reported and discussed an electrochemical energy storage system based on the Se\(^{2-}\)2Cu\(^{2+}\)+4e\(^-\)↔Cu\(_2\)Se redox reaction. The Se cathode undergoes a sequential conversion of Se↔ CuSe ↔ Cu\(_3\)Se\(_2\) ↔ Cu\(_2\)Se, following a four-electron transfer reaction and rendering a high theoretical specific capacity of 1350 mAh g\(_{\text{Se}}\)^\(-1\). Besides, the Se cathode chemistry shows a redox potential of 0.5 V vs. SHE, about 1.5 V higher than those in conventional Li/Na/K–Se batteries. It possesses fast reaction kinetics and shows promising prospect in fast-charging applications. There are still some limitations of this work, which need to be improved in future research. The electrochemical performance with a high Se areal loading (>15 mg cm\(^{-2}\)) requires further optimization. The anion-exchange membrane is required in Zn||Se@C-48 full cell, which leads high costs.
Methods

Materials. All materials, including selenium (Se) (Aladdin, 99.9%), CuSO₄ (Aladdin, 99.9%), ZnSO₄ (Aladdin, 99.5%), zinc foil (Suzhou Wingrise energy technology Co. Ltd., thickness: 0.05 mm, 99.99%), Cu foil (Guangdong Canid New Energy Technology Co., Ltd., thickness: 9 μm, 99.8%), carbon cloth (Suzhou Wingrise energy technology Co. Ltd., HCF330N, thickness: 0.33 ± 0.02 mm, 160 ~ 180 μm cm⁻²), stainless steel (Guangdong Canid New Energy Technology Co., Ltd., 400 mesh), porous carbon (Nanjing Momentum Materials Technologies Co., Ltd.), and anion-exchange membrane (fumasep, FAB-PK-130, Suzhou Wingrise energy technology Co. Ltd.), are used without further purification.

Characterization of materials. The morphology and microstructure analysis of the synthesized materials were examined using field-emission scanning electron microscopy (FESEM, Zeiss SUPRA™ 55 SAPPHIRE) and transmission electron microscopy (TEM, JEOL JEM 2010, USA). The composition of the products was analyzed by energy dispersive spectroscopy (EDS, EOL-6300F). The crystal structures were characterized by powder X-ray diffraction (XRD, Rigaku MiniFlex 600 diffractometer with Cu-Kα X-ray radiation, λ = 0.154056 nm). Raman spectra were performed by using a LabRAM HR Evolution (HORIBA Jobin Yvon, France) Raman microscope with a 532 nm laser. The content of Se in the prepared composites was estimated by Thermogravimetric analysis (TGA, Q50, USA) at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were conducted by Thermo Scientific ESCALAB 250Xi electron spectrometer. N₂ sorption isotherms were measured at 77 K on a KUBO X1000 sorption analyzer. The pore size distributions were calculated using the quenched solid density functional theory (QSDFT). For ex-situ XRD, TEM, and XPS measurements, the electrode samples were cut from Cu/0.5 M CuSO₄ | Se@C-48 coin cells. Typically, Cu/0.5 M CuSO₄ | Se@C-48 coin cells were performed CV tests at 0.02 mV s⁻¹ (negative scan from open-circuit voltage), disassembled after the first, second, third reduction peak, and full discharged state (0.01 V). The obtained cathodes were washed with water for three times and then dried under a vacuum at 60 °C for 12 h, which can then be used for various characterizations (XRD, TEM, and XPS). Sample holder with an inert atmosphere is not required during transport of the electrode samples to the equipment.

Synthesis of Se@C composite. The Se@C composite was obtained by a multielectron exchange method. Typically, the porous carbon and Se powder were first mixed with a certain mass ratio and then heated at 260 °C for 12 h in a tube furnace under an Ar atmosphere. The Se@C-48 composite was obtained at a Se-Carbon mass ratio of 50:50. Se@C-40, Se@C-65, and Se@C-78 composites were obtained at Se-carbon mass ratios of 45:55, 70:30, and 80:20, respectively. The Se content in Se@C composites is lower than the added Se because some Se lost during the heating process.

Electrochemical measurements. The cathode was prepared by a slurry coating procedure and carbon cloth was used as the current collector. Typically, Se@C, Super-P carbon black (Alfa Aesar, 99%), and polyvinylidene fluoride (PVDF) binders (Alfa Aesar) were added in N-Methyl-2-pyrrolidone (NMP, Aladdin, 99.9%), with a weight ratio of 80:10:10 to form slurry (using a mortar, in air) was then uniformly deposited onto a carbon cloth. The cathode was obtained after dried under vacuum at 60 °C for 12 h. The electrochemical performance of the Se@C-based composite working electrodes was investigated in CR2032 coin cell configuration using Cu foil as counter electrode and about 200 μL of 0.5 mol L⁻¹ CuSO₄ aqueous electrolyte solution. The copper anode also acts as the reference electrode and the electrode potential of the Cu²⁺/Cu is 0.33 V vs. standard hydrogen electrode (SHE). The electrochemical performance was tested on a Land tester (Wuhan Kingnuo Electronic Co., China), all cells were first discharged. The gravimetric specific capacities were calculated based on the mass of Se. The typical areal Se loading is about 2 mg cm⁻², and the typical electrode thickness (Se@C on carbon cloth) is about 350 μm. Higher areal Se loading of about 4, 8, 12 mg cm⁻² were also fabricated and tested for higher areal capacity. The Galvanostatic intermittent titration technique (GITT) test is performed by a series of galvanostatic charge or discharge pulses of 300 s at 500 mA g⁻¹ or charge pulses of 300 s at 500 mA g⁻¹ followed by 1800 s rest. Electrochemical impedance spectroscopy (EIS) was tested under AC amplitude of 5 mV at the frequency from 100 kHz to 1 Hz under the open-circuit potential (constant potential). The recording number of data points was 12 (per decade). The recording number of data points was 12 (per decade).

Calculation of theoretical volume expansion of Se cathode with different charge carriers. Taking Li-Se battery as an example. Li-Se batteries: Se + 2 Li⁺ + 2 e⁻ → Li₂Se

Assuming that there is 1 mol of Se cathode at the beginning, namely 78.9 g in mass. The density of Se is 4.8 g cm⁻³. So the volume of 1 mol of Se is about 78.9 g/4.8 g cm⁻³ = 16.44 cm⁻³. After discharging, theoretically, 1 mol of Se will convert into 1 mol of Li₂Se. The volume of 1 mol Li₂Se is (6.9 + 2 + 78.9) g/2.9 g cm⁻³ = 32 cm⁻³. Thus, the theoretical volume expansion of Se in Li-Se batteries is 32 cm⁻³/16.44 cm⁻³ ≈ 195%.

Calculation of the concentration of Se²⁻ ions in the four-electron Se chemistry. The solubility product constants (Ksp) of CuSe is 7.9 × 10⁻¹⁴. For CuSe, there exists the dissolution equilibrium of CuSe ↔ Cu²⁺ + Se²⁻. The concentration of Cu²⁺ is 0.5 mol/L. Therefore, the concentration of Se²⁻ ions is about 1.6 × 10⁻⁴ mol/L.

Calculation of the Cu²⁺ diffusion coefficient. It was based on the following equation:

\[ D = \frac{4}{\pi} \frac{m_Y V_Y}{M_X S} \left( \frac{\Delta E}{\Delta f} \right) \left( \tau + \frac{1}{2} \right) \]

where \( D \) is the Cu²⁺ diffusion coefficient; \( \Delta f \) is the charge or discharge pulses time (300 s); \( \Delta E \) is the cell voltage during charging or discharging at the time of current of flux; \( \tau \) is the thickness of the electrode.

Calculation of specific energy of Zn | Se@C-48 full cell. It was computed based on:

\[ E = \frac{Q_{\text{charge}} \times V_{\text{charge}} + Q_{\text{discharge}} \times V_{\text{discharge}}}{Q_{\text{charge}} + Q_{\text{discharge}}} \]

where \( E \) is specific energy (mWh g⁻¹); \( Q \) is the specific capacity of cathode (mAh g⁻¹); and \( V \) is the voltage of Zn | Se@C-48 full cell.

Calculation of energy efficiency of Zn | Se@C-48 full cell. The energy efficiency is energy efficiency; \( Q_{\text{charge}} \) and \( Q_{\text{discharge}} \) are specific capacities of discharge and charge process, respectively; and \( V_{\text{charge}} \) and \( V_{\text{discharge}} \) are the discharge voltage and charge voltage of Zn | Se@C-48 full cell.

First-principle calculations details. The projector augmented wave pseudopotential method implemented in the Vienna Ab initio Simulation Package (VASP) is used to perform structural relaxation and energy calculation. The energy cutoff and electronic self-consistent step convergence are set to be 300 eV and 10⁻⁶, respectively. In Fig. 5 the alloy volume deformation is adopted to simulate the lattice expansion or shrinking induced by Se expansion. This work is 290%, 418%, and 183%, respectively.

Data availability

All data generated in this study are provided in the Source Data file and its Supplementary Information. Source data are provided with this paper.

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Author contributions

L.Q. and Z.Z. led the team and supervised the experiments. C.D., H.C., Y.Z., Z.Z., and L.Q. conceived the idea. C.D., L.H., J.X., and Y.H. prepared materials and performed electrochemical measurements. C.D., Y.W., X.L., X.Z., and L.S. performed the characterizations (XRD, XPS, SEM, TEM, TGA, EIS) and analyzed the corresponding data. H.C. and M.X. contributed to in situ XRD. F.L. contributed to the theoretical calculations. All authors discussed the results and agreed on the submission of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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