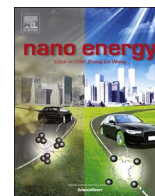




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## Atomic layer deposition-enabled ultrastable freestanding carbon-selenium cathodes with high mass loading for sodium-selenium battery

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## ABSTRACT

Melt diffusion followed by vapor deposition is judiciously combined with atomic layer deposition (ALD) to construct Al<sub>2</sub>O<sub>3</sub>-coated (Se/porous N-doped carbon nanofibers)@Se composite (denoted SC@Se-Al<sub>2</sub>O<sub>3</sub>) materials for sodium-selenium (Na-Se) batteries. High mass loading, ultrastable and free-standing carbon-selenium cathode is conveniently achieved by tailoring both the Se content and the thickness of deposited Al<sub>2</sub>O<sub>3</sub> layer. Importantly, in contrast to only 176 mAh g<sup>-1</sup> of the electrode without Al<sub>2</sub>O<sub>3</sub> deposition after 660 cycles, the composite with a Se content of 67 wt% and a 3-nm Al<sub>2</sub>O<sub>3</sub> thickness retains a reversible capacity of 503 mAh g<sup>-1</sup> after 1000 cycles with no capacity fading at 0.5 A g<sup>-1</sup>. These findings clearly suggest that ALD strategy provides a viable, controllable and effective means of tuning the electrode performance towards high mass loading of active materials and long cycle life of the resulting battery for energy storage applications.

## 1. Introduction

Sodium-selenium (Na-Se) batteries has recently received much attention for large-scale energy-storage applications as they possess high energy density and excellent safety and cyclic stability. They carry several advantageous attributes including low cost and wide availability of sodium resources [1–6], as well as their moderate theoretical gravimetric capacity (678 mA h g<sup>-1</sup>) and high volumetric capacity of Se (~3270 mAh cm<sup>-3</sup>). However, the polyselenide dissolution, poor electronic conductivity and inferior cycling stability are the challenges that plague the development of Na-Se batteries [7–12].

High specific energy densities are greatly desirable for developing practical energy storage devices. Therefore, the ability to construct cathodes with high Se loading is recognized as one of the essential steps towards building Na-Se batteries with optimized performance. However, the Se contents in the reported cathode composites are relatively low (30–54 wt%) [10–14], leading to a reduced specific energy density of the resulting Na-Se batteries. Moreover, additives such as carbon black and polymer binders are usually required to improve the mechanical integrity and electronic conductivity of electrodes, which

result in a further reduction in volumetric energy densities. Na-Se batteries with excellent mechanical flexibility, high specific energy density and excellent cyclic stability are highly beneficial for potential applications in wearable energy storage devices.

In this context, to achieve Na-Se batteries with long-term stability, strong chemical binding is required in order to prevent the dissolution of sodium polyselenides into electrolyte. Porous carbon can act as a conductive framework to entrap selenium, which promotes the reduction of polyselenide dissolution and improves the electronic conductivity of selenium [15–19]. The electronic and chemical properties of carbon framework can also be modulated by the introduction of heteroatoms via structure modification [20]. Moreover, it is important to note that metal oxides particles, such as Al<sub>2</sub>O<sub>3</sub> [21,22], TiO<sub>2</sub> [23] and SiO<sub>2</sub> [24], have been found to act as effective adsorbents for tethering the soluble polysulfides. However, such modifications are usually achieved by wet chemistry approaches, making it difficult to control the particle size and thus leading to incompact interfacial contacts between the components in batteries. Atomic layer deposition (ALD) technique has been widely employed in various fields including lithium ion batteries (LIBs) and SIBs [25–27], to render uniform thin film deposition

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on arbitrary surfaces.

Herein, we report on the judicious crafting of ALD-deposited, ultrastable and freestanding carbon-Se cathodes with high Se loading for Na-Se batteries. First, flexible and porous carbon nanofiber mats are produced by electrospinning and utilized as conductive matrix. Subsequently, high Se loading with tunable content up to 70 wt% is achieved by two consecutive Se infiltrations (i.e., melt diffusion and vapor deposition). A number of  $\text{Al}_2\text{O}_3$  layers are then deposited on the porous composite electrodes by ALD for effective prevention of polyselenide dissolution. Intriguingly, the  $\text{Al}_2\text{O}_3$  deposition leads to a negligible weight increase while the stability of electrode is significantly improved. It is worth noting that this is the first report of ALD-enabled Se-based cathode materials for Na-Se batteries. The effect of the  $\text{Al}_2\text{O}_3$  thickness deposited by ALD on the electrochemical performances of Na-Se batteries is systematically studied. Particularly, the electrode with 67 wt% of Se content and 25  $\text{Al}_2\text{O}_3$  layers exhibits an outstanding cyclic stability and electrochemical performance, and delivers an impressive specific capacity of  $503.5 \text{ mAh g}^{-1}$  after 1000 cycles at  $0.5 \text{ A g}^{-1}$  with a capacity retention of 71.2%. This is in sharp contrast to the 23.1% retention of the bare electrode (i.e., without ALD coating of  $\text{Al}_2\text{O}_3$ ) after 660 cycles, demonstrating its promising potential as an advanced cathode for Na-Se batteries.

## 2. Experimental

### 2.1. Preparation of the porous N-doped carbon nanofibers

The porous N-doped carbon nanofibers (PCNFs) were synthesized by using electrospinning technique combined with the carbonization process. (1) Typically, 1.4 g polyacrylonitrile (PAN) and 0.05 g F127 were dissolved into 15 mL dimethylformamide (DMF) organic solvent and stirred for at least 12 h to form a clear solution as the spinning solution. Then, the as-prepared solution was loaded into a 25 mL syringe pump, and the electrospinning process was conducted under 14.5 kV applied voltage and  $1.5 \text{ mL h}^{-1}$  feeding rate, as well as 15 cm collected distance. Finally, non-woven film can be easily peeled off from the collector and successively dried at  $80 \text{ }^\circ\text{C}$  under vacuum for 8 h. (2) Dried film was stabilized at  $280 \text{ }^\circ\text{C}$  for 4 h in air and then carbonized at  $850 \text{ }^\circ\text{C}$  for another 6 h at  $2 \text{ }^\circ\text{C min}^{-1}$  heating rate under  $\text{N}_2$  atmosphere.

### 2.2. Preparation of the (Se/PCNFs)@Se composite

The PCNFs were punched to disc with a 0.6 cm radius and mixed with Se powder. Subsequently, they were heated to  $260 \text{ }^\circ\text{C}$  for 12 h and then  $300 \text{ }^\circ\text{C}$  for 3 h in an Ar-filled tubular furnace to yield the Se/PCNFs (denoted SC) composite. After that, the SC composite and additional Se powder were respectively loaded in two sides of an alumina boat with a sealed cover and placed in a quartz tube reactor again, which was heated at  $350 \text{ }^\circ\text{C}$  for 2 h under flowing Ar gas, yielding (Se/PCNFs)@Se composite (denoted SC@Se).

### 2.3. Preparation of the $\text{Al}_2\text{O}_3$ -coated SC@Se composites by ALD

The  $\text{Al}_2\text{O}_3$  protective layer was directly grown on the freestanding SC@Se electrode using KE-MICRO PEALD-200A machine under  $4 \times 10^{-3}$  Torr at  $150 \text{ }^\circ\text{C}$ . Typically, trimethylaluminum (TMA, Fornano, 99.9999%) and deionized  $\text{H}_2\text{O}$  were used as the aluminum and oxygen source, respectively. Ar (99.999%) gas was used as the carrier gas with a flow rate of 20 sccm. Typically, a complete atomic layer deposition (ALD) cycle consisting of a sequential and alternating supply of TMA and  $\text{H}_2\text{O}$  as follows: a 0.05 s supply of TMA vapor, a 7 s exposure of TMA to the electrodes, a 60 s-Ar purge, a 0.06 s supply of water vapor, a 7 s extended exposure of  $\text{H}_2\text{O}$  to the electrodes, and 70 s-Ar purge. The ALD process were conducted for 0, 10, 25, 40 cycles to produce a series of the  $\text{Al}_2\text{O}_3$ -coated SC@Se composites (denoted SC@Se- $x\text{Al}_2\text{O}_3$

composites; where  $x = 0, 10, 25,$  and  $40$  cycles). It is notable that the content of  $\text{Al}_2\text{O}_3$  was difficult to be accurately measured in the composite due to its ultrasmall amount.

### 2.4. Physical characterizations

The morphology and microstructure of SC@Se- $x\text{Al}_2\text{O}_3$  composites were examined by FESEM (JSM-7800F & TEAM Octane Plus) and HRTEM (Tecnai G2 F30). The structure and Raman spectrum were collected on X-ray diffraction (Bruker, D8 Advance with Cu-K $\alpha$  radiation) and Raman microscope (DXR Thermo-Fisher Scientific), respectively. Thermogravimetric analysis (TGA-Q50) was performed under nitrogen atmosphere from room temperature up to  $700 \text{ }^\circ\text{C}$  with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . BELSORP-max Surface Area and Porosimetry instrument was used to measure the nitrogen adsorption/desorption isotherms of electrodes. X-ray photoelectron spectroscopy (XPS) tests were carried out using an ESCALAB 250Xi system, and all data were calibrated using adventitious C1s peak at a fixed value of 284.4 eV. To prepare HRTEM samples, a trace amount of samples were added into ethanol solution with ultrasonic dispersion for 1 h, and then dropped to the micro Cu grid and dried.

### 2.5. Electrochemical measurements

The electrochemical tests were performed with CR2032 coin-type cells, which were assembled with sodium metal as the counter and reference electrodes inside an argon-filled glove box (MBRAUN, UNILab2000, both moisture and oxygen levels below 1 ppm). Glass fiber (Whatman) was used as the separator. The electrolyte was 1 M of  $\text{NaClO}_4$  in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v). The freestanding SC@Se- $x\text{Al}_2\text{O}_3$  composites were directly used as the working electrodes without any other binders and carbon conductors. The loading mass of the active material was  $1.2\text{--}1.6 \text{ mg cm}^{-2}$ . The galvanostatic charge-discharge tests were carried out over a voltage range of 1.0–3.0 V (vs.  $\text{Na}^+/\text{Na}$ ) on a battery test system (Land, CT-2001A) ( $1 \text{ C} = 675 \text{ mA g}^{-1}$ ). Electrochemical impedance spectroscopy (EIS) measurements were performed using the electrochemical workstation (CHI760D) by applying a voltage of 5 mV over a frequency of  $10^{-2}\text{--}10^5$  Hz. All the cells were held at ambient temperature for at least 8 h before tests. All the specific capacity in this study was calculated on the basis of the selenium mass loading. For the ex-situ SEM tests, all procedures were performed in a glove box filled with argon, and tested electrodes were carefully washed with DEC solvent for three times and dried.

## 3. Results and discussion

Fig. 1a illustrates the step-wise preparation procedure for SC@Se- $x\text{Al}_2\text{O}_3$  composites. Notably, the intensive chemical activation was found to cause a large specific surface area that renders a high Se loading. However, it also led to a poor conductivity and a low mechanical strength of the carbon matrix [9–12]. To address this unfavorable issue, the freestanding porous PCNFs were produced by electrospinning, followed by the carbonization process without further chemical activation (1st panel in Fig. 1a; see Section 2). The SC composites were first formed via a simple melt-diffusion of elemental Se (2nd panel in Fig. 1a). Specifically, the solid Se powder tended to melt and diffuse into the mesoporous carbon matrix during this process. The successful diffusion was substantiated as discussed later. The composites were then further treated with the different mass ratio of Se powder by vapor deposition to create the SC@Se composites (3rd panel in Fig. 1a). Finally, the  $\text{Al}_2\text{O}_3$  protective layers with nanometer thickness were directly deposited onto the SC@Se composites using ALD process, where a number of ALD cycles were applied to yield the  $\text{Al}_2\text{O}_3$  coating with varied thickness (4th panel in Fig. 1a).

The PCNFs clearly exhibit a continuous and interconnected

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