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Flexible ReS<sub>2</sub> nanosheets/N-doped carbon nanofibers-based paper as a universal anode for alkali (Li, Na, K) ion batteryMinglei Mao<sup>a,b</sup>, Chunyu Cui<sup>b</sup>, Mingguang Wu<sup>b</sup>, Ming Zhang<sup>b</sup>, Tao Gao<sup>a</sup>, Xiulin Fan<sup>a</sup>, Ji Chen<sup>a</sup>, Taihong Wang<sup>b</sup>, Jianmin Ma<sup>b</sup>, Chunsheng Wang<sup>a,\*</sup><sup>a</sup> Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, United States<sup>b</sup> School of Physics and Electronics, Hunan University, Changsha 410082, China

## ARTICLE INFO

## Keywords:

Universal anode

ReS<sub>2</sub>

N-doped carbon nanofibers

Alkali (Li, Na, and K) ion battery

## ABSTRACT

Alkali (Li, Na, K) ion battery have practically or potentially been widely used as a power source for portable electronic devices and electric vehicles. However, lack of universal anodes for these three alkali ion battery are restricting their development, especially for Na-ion battery and K-ion battery. Rhenium disulfide (ReS<sub>2</sub>), with large interlayer space and weak van der Waals interaction between layers, can afford massive alkali (lithium, sodium, and potassium) ions to diffuse easily between the layers. However, its low electronic conductivity and large volume changes in the conversion reaction significantly compromise the cycle life. To address this issue, here, we anchor ReS<sub>2</sub> nanosheets onto nitrogen doped carbon nanofibers (N-CNF) which forms a flexible ReS<sub>2</sub>/N-CNFs paper for alkali (Li, Na, and K) ion battery anodes. The carbon nanofibers (CNFs) can improve the conductivity and the doped nitrogen can absorb sulfur and polysulfide generated by the conversion reaction. As a result, the ReS<sub>2</sub>/N-CNFs composite anode maintains a reversible capacity of 430 mAh/g after 400 cycles at 100 mA/g in LIBs, 245 mAh/g after 800 cycles at 100 mA/g in NIBs, and 253 mAh/g after 100 cycles at 50 mA/g in KIBs. This performance is one of the best among all ReS<sub>2</sub> reported up to date. In addition, the solid electrolyte interface formation on ReS<sub>2</sub> and the coulombic efficiency in different alkali ion batteries are also systemically investigated.

## 1. Introduction

Because of the high energy density and long cycle life, lithium ion batteries (LIBs) have been widely used in portable electronics and power electric vehicles (EVs) [1–3]. Nevertheless, the currently commercialized LIBs cannot meet the growing demand for these electronic devices on energy and power. Due to the limited lithium supply, sodium ion batteries (NIBs) have attracted intensive interests as an alternative to LIBs for applications where cost is an important factor [4,5]. Nevertheless, the energy density of NIB is lower than that of LIB due to relatively high standard potential of sodium (−2.71 V vs. E°) compared to lithium (−3.04 V vs. E°) [6,7]. Another promising alternative for low cost application is potassium ion batteries (KIBs) due to natural abundance and suitable potential (−2.93 V vs. E°) closed to lithium [8–10]. These three alkali ion batteries are complementary and suitable for different applications. Over the past two decades, graphite has been the most widely used anode for LIBs. However, graphite suffers from low capacity and poor rate performance as Li-ion battery anodes (372 mAh/g) [3,11,12], and it is not suitable for NIB anodes [13], and also has a

low capacity for KIBs (279 mAh/g) [14,15]. Thus, exploring a universal high capacity electrode material that is suitable for these three alkali ion batteries are of practical importance.

2D transition metal dichalcogenides (TMDs) compounds that are composed of group VI transition metals (Mo, W, or Re) and chalcogens (S or Se) have received surging research interests as anode candidates for alkali ion batteries [16–20]. Rhenium disulfide (ReS<sub>2</sub>), as a new member of TMDs family, have inherent anisotropy and much weaker interlayer coupling resulting from additional valence electron in rhenium [21–23]. As the anode material for LIB, it has a theoretical capacity of 430 mAh/g due to its 4-electron transfer reaction [16,24,25]. In addition, ReS<sub>2</sub> possesses much less coupling energy (~18 meV per unit cell) compared to MoS<sub>2</sub> (~460 meV) [26], although their interlayer spacing are comparative (6.14 Å for ReS<sub>2</sub> and 6.15 Å for MoS<sub>2</sub>) (Fig. S1a, b) [16]. The large interlayer spacing and extremely weak van der Waals attraction between layers allow the facile diffusion of alkali metal ions within layers. This feature enables ReS<sub>2</sub> to be a natural candidate as a universal anode material for all alkali ion batteries. However, the low conductivity and poor cycling performance of ReS<sub>2</sub>

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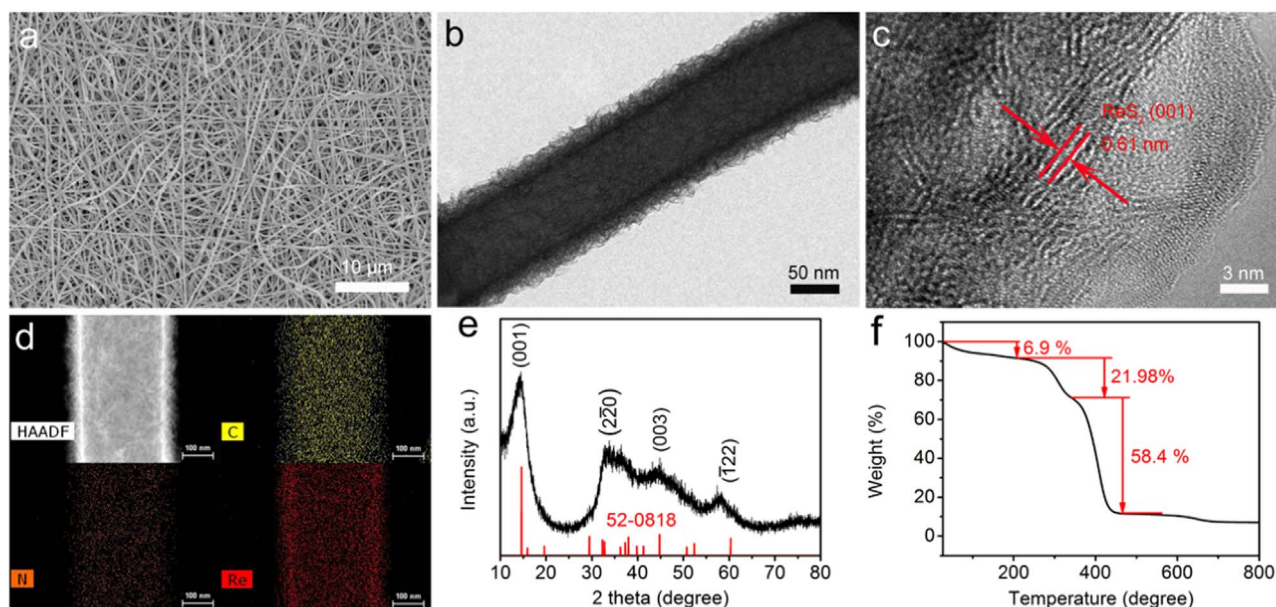


Fig. 1. (a) SEM of  $\text{ReS}_2/\text{N-CNFs}$ . (b) TEM and (c) HR-TEM images of  $\text{ReS}_2/\text{N-CNFs}$ . (d) TEM observation and corresponding EDS elemental mapping of carbon, nitrogen, and rhenium. (e) XRD pattern and (f) TGA curve of  $\text{ReS}_2/\text{N-CNFs}$  in air at a rate of  $5^\circ\text{C}/\text{min}$ .

severely restrict its application in batteries [27,28]. Despite the conductivity of  $\text{ReS}_2$  can be enhanced by mixing with carbon conductive network [28–30], capacity fading has not been resolved, because  $\text{Li}_2\text{S}_x$  produced by the conversion reaction of  $\text{ReS}_2$  during cycling dissolve in the electrolyte and cause active materials loss.

Herein, we proposed a novel  $\text{ReS}_2$  composites to solve the aforementioned low conductivity and polysulfide dissolution problem simultaneously. The  $\text{ReS}_2$  nanosheets is anchored on N-doped carbon nanofibers ( $\text{ReS}_2/\text{N-CNFs}$ ) with a facile electrospinning and hydrothermal method, which not only provides electronic conductivity but also offer chemical adsorption to the formed polysulfide. Combining all the advantages of the composite anode (the large interlayer spacing and extremely weakly van der Waals interaction of  $\text{ReS}_2$ , high conductivity, oriented electronic/ionic transport pathway of CNFs, and strong absorption of nitrogen doping to sulfur and polysulfide) [31,32], the  $\text{ReS}_2/\text{N-CNFs}$ -based paper show outstanding electrochemical performance in LIBs, NIBs, and KIBs, demonstrating its supremacy as a universal anode materials for these alkali ion batteries.

## 2. Experimental section

### 2.1. Preparation of $\text{ReS}_2/\text{N-CNFs}$

0.43 g polyacrylonitrile (PAN) was added into 6 mL N, N-dimethyl formamide and stirred for 2 h in  $60^\circ\text{C}$  to obtain the transparent solution. Then, the precursor solution was transferred into a 20 mL syringe with a stainless steel needle (with 0.71 mm inner diameter). A syringe pump controlled the flow rate to about 0.2 mL/h. A piece of aluminum foil used as the collector was vertically positioned about 15 cm away from the needle. A high voltage DC power supply of 11–14 kV between needle and aluminum foil was obtained. After pre-oxidation of the obtained nanofibers at  $230^\circ\text{C}$  in air for 6 h, the brown mats were treated at  $720^\circ\text{C}$  in argon for 2 h to get the N-doped CNFs [33].

66 mg  $\text{NH}_4\text{ReO}_4$  and 120 mg thioacetamide ( $\text{C}_2\text{H}_5\text{NS}$ ) were dissolved in 40 mL  $\text{H}_2\text{O}$ . After stirring for 10 min, 0.2 g hexamethylenetetramine was added to form a transparent solution. Then, 40 mg N-doped CNFs was immersed in the above solution. The solution was transferred into a Teflon-lined autoclave and maintained at  $220^\circ\text{C}$  for 48 h. After cooling to room temperature,  $\text{ReS}_2/\text{N-CNFs}$  was rinsed with distilled water and ethanol for several time, and dried in a vacuum oven

at  $60^\circ\text{C}$  overnight. For comparison, pure  $\text{ReS}_2$  was prepared under the same condition without the presence of N-doped CNFs.

### 2.2. Material Characterizations

Field emission scanning electron microscopy (FESEM, Model JSM-7600F, JEOL Ltd., Tokyo, Japan) was used to characterize the morphologies and size of the synthesized samples. The chemical composition was investigated by the energy dispersive X-ray spectroscopy (EDS). High resolution transmission electron microscopy (HRTEM) images were carried out with a JOEL JEM 2100F microscope. X-ray powder diffraction (XRD) patterns were recorded on a Bruke D8 Advance powder X-ray diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 0.15406\text{ nm}$ ). X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250. Thermogravimetric analysis (TGA) was measured from  $30$  to  $800^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  under 100 mL/min of flowing air with a Perkin-Elmer TGA 4000.

### 2.3. Electrochemical measurements

The final  $\text{ReS}_2/\text{N-CNFs}$  was cut into pieces with size of  $5 \times 5\text{ mm}^2$  and directly used as anodes, each of which weigh  $\sim 1\text{ mg}$ . Electrochemical performance was tested in CR2032 coin cells, which were assembled in an argon-filled glove box with lithium, sodium, and potassium foil as the counter electrode, 1 M bis(trifluoromethane) sulfonamide lithium salt ( $\text{LiTFSI}$ , Sigma Aldrich) in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v, 1:1), 1 M  $\text{NaSO}_3\text{CF}_3$  in diglyme, and 0.8 M  $\text{KTFSI}$  in DME as the electrolyte, respectively, and Celgard 2400 microporous polypropylene membrane as separators. Electrochemical performance was tested using an Arbin battery test station (BT2000, Arbin Instruments, USA) at various current rates with voltage cutoff of 0.01–3 V. Capacity was calculated on the basis of total mass of the entire  $\text{ReS}_2/\text{N-CNFs}$ . CV curves were recorded at a scan rate of 0.1 mV/s using an electrochemical work station. Nyquist plots were recorded using a Zahner IM6 electrochemical work station at a frequency range of 0.01–100 kHz.

## 3. Results and discussion

As shown in the scanning electron microscope (SEM) images in

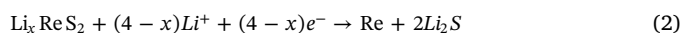
Fig. 1a and Fig. S2a, the flexible  $\text{ReS}_2/\text{N-CNFs}$  paper consists of uniform straight nanofibers with a diameter of 200–400 nm. The interconnected conductive N-doped CNFs network favors fast electronic transportation. Such long fiber and interconnected structure ensure the excellent mechanical property (Fig. S3) and stability of  $\text{ReS}_2/\text{N-CNFs}$  paper during electrochemical processes. Whereas, pure  $\text{ReS}_2$  forms anomalous spheres with diameter up to micrometer (Fig. S2b), which will cause slow kinetics for ions to diffuse into. Consistent with SEM results, a low-resolution TEM image (Fig. 1b) shows that  $\text{ReS}_2$  nanosheets evenly anchor on the surface of N-doped CNFs with the diameter of ~200 nm. The specific surface area of  $\text{ReS}_2/\text{N-CNFs}$  is  $\sim 95.21 \text{ m}^2/\text{g}$  by BET (Fig. S2c). From the high-resolution TEM (HR-TEM) image (Fig. 1c), (001) crystal facet of  $\text{ReS}_2$  with layer space of 0.61 nm can be clearly observed. Besides, the energy dispersive X-ray spectroscopy (EDS) elemental mapping images (Fig. 1d) well match results shown in Fig. 1b. It is shown that nitrogen is evenly doped in the CNFs, while rhenium and sulfur constitute  $\text{ReS}_2$  uniformly anchored on the surface of N-doped CNFs.

The structure and composition of  $\text{ReS}_2/\text{N-CNFs}$  are characterized by X-ray diffraction (XRD) and thermogravimetric analysis (TGA), respectively. As shown in Fig. 1e, all the main peaks in the pattern can be indexed to  $\text{ReS}_2$  (JCPDS card No. 52-0818). No peaks for graphite is present, suggesting that carbon exists in amorphous state due to low calcination temperature [33]. The mass loading of  $\text{ReS}_2$  in  $\text{ReS}_2/\text{N-CNFs}$  was measured using TGA (Fig. 1f). A mass loss of ~6.9% below 150 °C could be attributed to the loss of physically absorbed water. The weight loss of 21.98% at around 200–350 °C can be ascribed to the oxidation of  $\text{ReS}_2$ , corresponding to 23.75% of  $\text{ReS}_2$  in  $\text{ReS}_2/\text{N-CNFs}$ . Moreover, an obvious weight loss of 58.4% arises from 350 to 480 °C, which can be ascribed to the oxidation of N-doped CNFs [34]. In addition, components of  $\text{ReS}_2/\text{N-CNFs}$  can be further confirmed by energy-dispersive spectrometry (EDS) in Fig. S4a.

X-ray photoelectron spectroscopy (XPS) was conducted to identify the chemical status of elements in  $\text{ReS}_2/\text{N-CNFs}$  (Fig. 2). Fig. 2a shows XPS survey spectra of  $\text{ReS}_2/\text{N-CNFs}$ , from which peaks of C 1s, N 1s,

and Re 4f can be clearly observed. Fig. 2b exhibits a high-resolution C 1s XPS spectrum of  $\text{ReS}_2/\text{N-CNFs}$ . Two peaks centered at 284.8 and 286.1 eV can be assigned to extensively delocalized sp<sup>2</sup>-hybridized carbon atoms and the carbon-nitrogen bond, respectively [35,36]. The high-resolution N 1s XPS spectrum can be assigned to a pyrrolic nitrogen (a trigonal nitrogen phase bonded to a sp<sup>2</sup>-coordinated carbon) with binding energy of 401.0 eV and a classic graphitic-type quaternary nitrogen with binding energy of 402.3 eV (Fig. 2c) [37,38]. The N content in N-CNFs is ~11 at%. The high-resolution Re 4f XPS spectrum of  $\text{ReS}_2/\text{N-CNFs}$  exhibit two peaks at 42.7 and 45.1 eV, which can be attributed to the Re 4f<sub>7/2</sub> and Re 4f<sub>5/2</sub> spin orbit peaks of  $\text{ReS}_2$ , respectively (Fig. 2d). In addition, two S 2p peaks at 163.2 and 164.3 eV further confirm the presence of  $\text{ReS}_2$  (Fig. S4b). The XPS results corroborate the existence of  $\text{ReS}_2$  and N-doped CNFs, which agrees well with the XRD results.

The electrochemical performance of  $\text{ReS}_2/\text{N-CNFs}$  anode in Li-ion batteries was evaluated in coin-type cells by directly using flexible  $\text{ReS}_2/\text{N-CNFs}$  paper as working electrodes and Li metal as a counter electrode (Fig. 3). Cyclic voltammetry (CV) curves of  $\text{ReS}_2/\text{N-CNFs}$  were conducted at the scan rate of 0.1 mV/s between 0.01 and 3 V (Fig. 3a). In the first cathodic scan, two dominant reduction peaks at ~1.32 and 0.71 V can be clearly seen. The peak at 1.32 V is ascribed to insertion of  $\text{Li}^+$  into the layer space of  $\text{ReS}_2$  to form  $\text{Li}_x\text{ReS}_2$  according to the reaction (1) [28,29,39]. The followed wide peak centered at 0.71 V is due to the formation of SEI and the reduction of  $\text{Li}_x\text{ReS}_2$  to  $\text{Li}_2\text{S}$  and metallic Re by a conversion reaction according to the reaction (2) [29,39]. In the following anodic scan, a peak centered at 1.83 V is associated with the delithiation of  $\text{Li}_2\text{S} + \text{Re}$  composite into  $\text{Li}_x\text{ReS}_2$ , followed by a distinct peak located at 2.33 V which is contributed by the formation of  $\text{ReS}_2$  [29,40].



During the 2nd and 3rd cycle, the reduction peaks at 1.32 V and 0.71 V shift to ~2 V and 1.23 V due to relaxation of stress and strain in

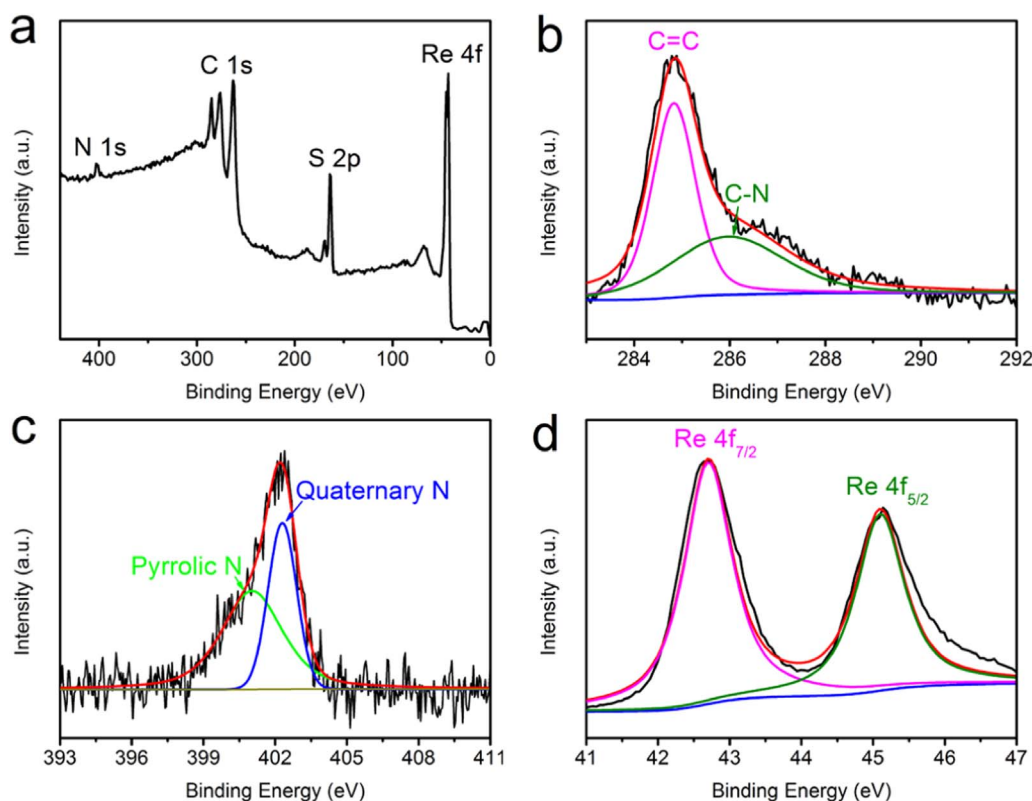
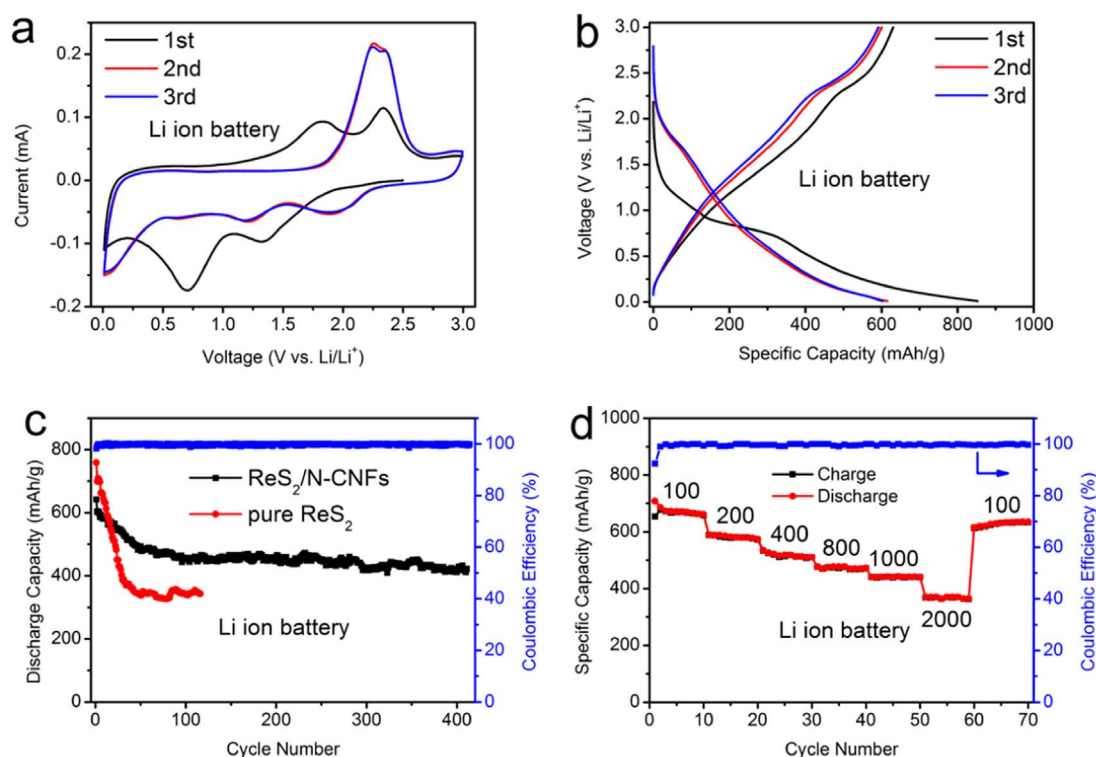
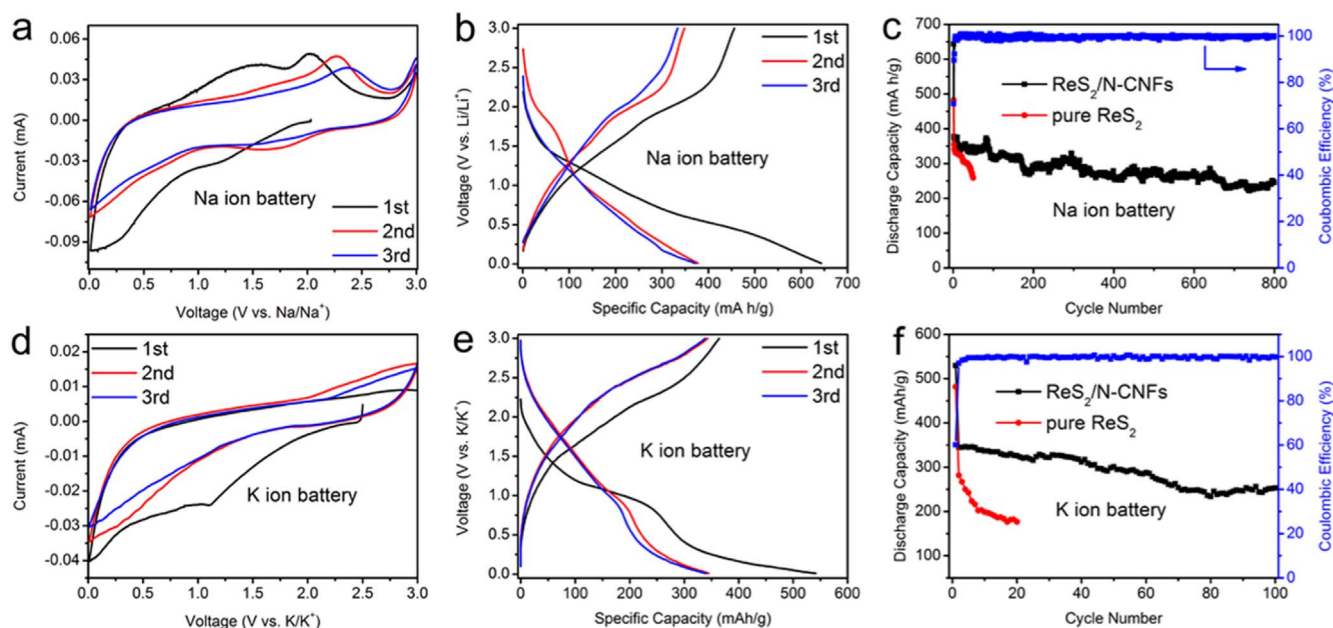


Fig. 2. (a) Survey XPS spectra of  $\text{ReS}_2/\text{N-CNFs}$ . (b-d) High-resolution XPS spectra of C 1s, N 1s, and Re 4f, respectively.



**Fig. 3.** Electrochemical performance of  $\text{ReS}_2/\text{N-CNFs}$  as a Li-ion battery anode. (a) Cyclic voltammetry curves of  $\text{ReS}_2/\text{N-CNFs}$  at a scan rate of 0.1 mV/s. (b) Galvanostatic discharge-charge profiles of  $\text{ReS}_2/\text{N-CNFs}$  for the first three cycles at a current density of 100 mA/g. (c) Cycling performance of the electrodes based on  $\text{ReS}_2/\text{N-CNFs}$  and pure  $\text{ReS}_2$  at a current density of 100 mA/g. (d) Rate performance of  $\text{ReS}_2/\text{N-CNFs}$  at different current density (mA/g). The capacity of  $\text{ReS}_2/\text{N-CNFs}$  is based on the mass of entire electrodes.



**Fig. 4.** Electrochemical performance of  $\text{ReS}_2/\text{N-CNFs}$  anode in Na-ion and K-ion batteries. (a-c) Cyclic voltammetry curves, galvanostatic discharge-charge profiles, and cycling performance of  $\text{ReS}_2/\text{N-CNFs}$  in NIBs, respectively. (d-f) Cyclic voltammetry curves, galvanostatic discharge-charge profiles, and cycling performance of  $\text{ReS}_2/\text{N-CNFs}$  in KIBs, respectively. The capacity of  $\text{ReS}_2/\text{N-CNFs}$  is based on the mass of entire electrodes.

the first charge/discharge cycle, while the delithiation of  $\text{Li}_2\text{S} + \text{Re}$  composite at 1.83 V also shift and merge with delithiation peak of  $\text{Li}_x\text{ReS}_2$  at 2.33 V.

The Galvanostatic discharge and charge curves of  $\text{ReS}_2/\text{N-CNFs}$  in LIBs in the first three cycles at a current density of 100 mA/g between 0.01 and 3 V are shown in Fig. 3b. There are two main plateau in the first discharge and charge curves, which is in accordance with the CV profiles. The first discharge and charge capacities of  $\text{ReS}_2/\text{N-CNFs}$  are

852 and 630 mAh/g, corresponding to the Coulombic Efficiency (CE) of 73.9%. The irreversible capacity can be mainly ascribed to the inevitable decomposition of electrolyte to form solid-electrolyte interphase (SEI) and irreversible conversion reaction in the first cycle [33,41]. The overlap of discharge and charge curves in the following two cycles implies the high cycling stability of  $\text{ReS}_2/\text{N-CNFs}$ .

The cycling performance of  $\text{ReS}_2/\text{N-CNFs}$  was evaluated at a current density of 100 mA/g (Fig. 3c).  $\text{ReS}_2/\text{N-CNFs}$  show a high capacity

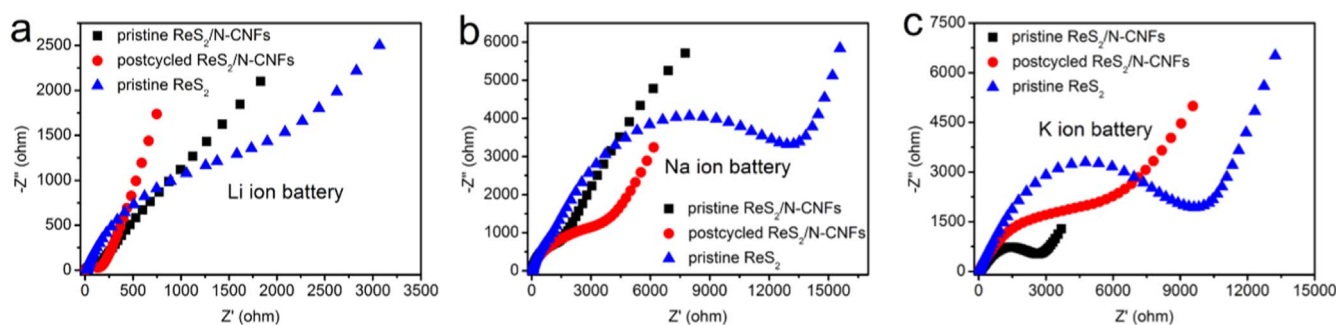


Fig. 5. (a–c) Nyquist plot of  $\text{ReS}_2/\text{N-CNFs}$  and pure  $\text{ReS}_2$  before and after 100 cycles in LIBs, NIBs, and KIBs, respectively.

retention and good cycling stability, which can be attributed to the high conductivity of flexible N-doped CNFs paper and the strong absorption of nitrogen doping to lithium polysulfide. Even after 400 cycles, the reversible capacity of  $\text{ReS}_2/\text{N-CNFs}$  can be kept at 440 mA h/g after initial drop, which is more stable than  $\text{ReS}_2$ -based anodes previously reported (Table S1). In addition, the CE of  $\text{ReS}_2/\text{N-CNFs}$  maintains beyond 99.5% after the first 10 cycles, which is indicative of good cycling stability. In contrast, the capacity of pure  $\text{ReS}_2$  quickly drops to around 340 mA h/g within 50 cycles, highlighting the contribution of N-doped CNFs to excellent cycling performance. Also, the cycling performance of N-CNFs for LIBs is conducted, which delivers the capacity of 232 mA h/g after 100 cycles (Fig. S4c). The rate performance of the as-synthesized  $\text{ReS}_2/\text{N-CNFs}$  in LIBs is shown in Fig. 3d. At a low current density of 100 mA/g,  $\text{ReS}_2/\text{N-CNFs}$  delivers a high discharge capacity of 660 mA h/g. When the current densities gradually increase from 200, 400, 800, 1000, to 2000 mA/g, corresponding capacities can maintain 580, 520, 470, 440, and 360 mA h/g, respectively. Then the capacity can recover to 630 mA h/g, when the current density is reduced to 100 mA/g. The results demonstrate that  $\text{ReS}_2/\text{N-CNFs}$ -based paper is a promising anode candidate for LIBs.

The sodium- and potassium-storage performances of  $\text{ReS}_2/\text{N-CNFs}$  were also evaluated in coin cells (Fig. 4). CV of  $\text{ReS}_2/\text{N-CNFs}$  for NIBs was conducted at a scan rate of 0.1 mV/s between 0.01 and 3 V (Fig. 4a). In the first cathodic scan, two peaks at 1.2 and 0.3 V can be attributed to insertion of  $\text{Na}^+$  into the interlayer space of  $\text{ReS}_2$  to form  $\text{Na}_x\text{ReS}_2$ , and reduction of  $\text{Na}_x\text{ReS}_2$  into  $\text{Na}_2\text{S}$  and metallic Re by a conversion reaction, respectively. In the following anodic scan, a peak centered at 1.5 V is associated with the desodiation of  $\text{Na}_2\text{S} + \text{Re}$  composite into  $\text{Li}_x\text{ReS}_2$ , followed by a distinct peak located at 2 V, which can be attributed to the formation of  $\text{ReS}_2$ .

Galvanostatic discharge-charge profiles of  $\text{ReS}_2/\text{N-CNFs}$  for the first three cycles at a current density of 100 mA/g between 0.01 and 3 V in NIBs are shown in Fig. 4b. The first discharge and charge capacities are 643 and 456 mA h/g, respectively, corresponding to CE of 70.9%, which is lower than that in LIBs, probably due to more reduction of electrolyte to form SEI in NIBs. In the following cycles, higher CE is obtained, reaching 92.3% in the third cycle, indicating highly reversible capacity. Besides, plateaus in the discharge-charge curves are in accordance with peaks in the CV. The cycling performance of  $\text{ReS}_2/\text{N-CNFs}$  in NIBs was measured at a current density of 100 mA/g between 0.01 and 3 V (Fig. 4c).  $\text{ReS}_2/\text{N-CNFs}$  shows a very stable long-term cycle life. The reversible capacity can maintain 300, 263, 245 mA h/g after 200, 400, and 800 cycles, respectively, with a slight decrease. Remarkably, the CE approaches above 99.5%, implying that superior cycle stability of  $\text{ReS}_2/\text{N-CNFs}$  electrode for reversible  $\text{Na}^+$  storage was highly repeatable. In contrast, the capacity of pure  $\text{ReS}_2$  falls dramatically to  $\sim 260$  mA h/g within first 50 cycles, which shares the same trend with that in LIBs. Still, the cycling performance of N-CNFs for NIBs is investigated, which delivers a capacity of 204 mA h/g (Fig. S4c).

The CV of  $\text{ReS}_2/\text{N-CNFs}$  in KIBs was tested at a scan rate of 0.1 mV/s between 0.01 and 3 V (Fig. 4d). Based on the similar reaction

mechanism with that in LIBs and NIBs, during the first cathodic cycle,  $\text{ReS}_2$  hold  $\text{K}^+$  within layers and then is reduced to metallic Re embedded in the matrix of  $\text{K}_2\text{S}$ . In the following anodic scan, Re and  $\text{K}_2\text{S}$  are oxidized to  $\text{ReS}_2$ .

Galvanostatic discharge-charge curves of  $\text{ReS}_2/\text{N-CNFs}$  for KIBs in the first three cycles at a current density of 50 mA/g between 0.01 and 3 V are shown in Fig. 4e. In the first cycle, discharge and charge capacity are 541, and 364 mA h/g, respectively, corresponding to CE of 67.3%. The CE of  $\text{ReS}_2/\text{N-CNFs}$  in the first cycle decreases from that in LIBs (73.9%), NIBs (70.9%), to KIBs (67.3%), which can be on account of different consumption of electrolyte on forming SEI and diverse electrochemical reversibility of alkali metal sulfide ( $\text{Li}_2\text{S}$ ,  $\text{Na}_2\text{S}$ , and  $\text{K}_2\text{S}$ ). Cycling performance of  $\text{ReS}_2/\text{N-CNFs}$  for KIBs was evaluated at a current density of 50 mA/g between 0.01 and 3 V (Fig. 4f). After 100 cycles,  $\text{ReS}_2/\text{N-CNFs}$  can obtain a discharge capacity of 253 mA h/g, superior to many reported anodes for KIBs [9,42,43]. Besides, CE of  $\text{ReS}_2/\text{N-CNFs}$  reaches 99% beyond the 5th cycle. In addition,  $\text{ReS}_2/\text{N-CNFs}$  tend to sustain the origin morphology even after 100 cycles in LIBs, NIBs, and KIBs (Fig. S5), indicating importance of flexible and tough N-doped CNFs to keep the structure intact. It is clear that SEI on the surface of  $\text{ReS}_2/\text{N-CNFs}$  is thicker after cycling in NIBs and KIBs than that in LIBs, which is in accordance with lower CE for the first cycle in NIBs and KIBs. By contrast, discharge capacity of pure  $\text{ReS}_2$  drops sharply to below 200 mA h/g within 20 cycles, even though the capacity of N-CNFs can sustain 191 mA h/g after 100 cycles (Fig. S4c). Cycling deterioration of  $\text{ReS}_2/\text{N-CNFs}$  in KIBs compared to that in LIBs and NIBs could be attributed to more severe volume variation caused by conversion reaction and inferior electrochemical reversibility of  $\text{K}_2\text{S}$ .

To better understand the enhancement of N-CNFs to the electrochemical performance of  $\text{ReS}_2$ , electrochemical impedance spectra (EIS) of  $\text{ReS}_2/\text{N-CNFs}$  and pure  $\text{ReS}_2$  before and after 100 cycles in LIBs, NIBs, and KIBs were carried out (Fig. 5). All the EIS are composed of a depressed semicircle in the high frequency region contributed by SEI resistance ( $R_{\text{SEI}}$ ) and charge-transfer resistance ( $R_{\text{ct}}$ ) and a sloping straight line in the low frequency region related with ion diffusion process called Warburg impedance. Comparing EIS of pristine  $\text{ReS}_2/\text{N-CNFs}$  and  $\text{ReS}_2$  in LIBs (Fig. 5a),  $R_{\text{ct}}$  for  $\text{ReS}_2/\text{N-CNFs}$  is much smaller than that for pure  $\text{ReS}_2$ , indicating that N-doped CNFs contribute to the fast charge-transfer process. Meanwhile,  $R_{\text{ct}}$  and  $R_{\text{SEI}}$  of  $\text{ReS}_2/\text{N-CNFs}$  increase after cycling in LIBs, probably attributed to formation of stable SEI and a phase transformation during conversion reaction. The same trend can be observed in the EIS of  $\text{ReS}_2/\text{N-CNFs}$  and pure  $\text{ReS}_2$  for NIBs and KIBs (Fig. 5b and c), which further confirms that N-doped CNFs contribute much to the improved electrochemical performance of  $\text{ReS}_2/\text{N-CNFs}$  in LIBs, NIBs, and KIBs. The flexible N-doped CNFs network can provide fast electron transfer and prohibit the intermediate products aggregated. In addition, the nitrogen doping in N-doped CNFs can absorb S and polysulfide generated during conversion reaction to prevent them aggregated and dissolved in the electrolyte [31,32]. Furthermore, it can be clearly seen that  $R_{\text{SEI}}$  and  $R_{\text{ct}}$  of postcycled  $\text{ReS}_2/\text{N-CNFs}$  increase from in LIBs, NIBs to KIBs, which is in accordance with their

gradually reduced CE for the first cycle. It may be related with the different thickness of SEI layers, kinetics of various ion diffusing across SEI and in the active materials in LIBs, NIBs, and KIBs. To be specific, due to greater volume change of  $\text{ReS}_2/\text{N-CNFs}$  in KIBs, thicker SEI form on the surface of active materials. Meanwhile, because of larger  $\text{K}^+$  diameter, it is more difficult for  $\text{K}^+$  to cross the SEI layer in KIBs. Additionally, diffusion barrier of  $\text{K}^+$  in active materials is higher than that in LIBs and NIBs. All of these reasons contribute to the greater  $R_{\text{SEI}}$  and  $R_{\text{ct}}$  in KIBs than that in LIBs and NIBs. More precise and deep analysis are under further investigation.

In summary, a universal anode based on the flexible  $\text{ReS}_2/\text{N-CNFs}$ -based paper was synthesized by a facile electrospinning and hydrothermal method and used as binder- and current collector-free anodes for alkali ion battery.  $\text{ReS}_2/\text{N-CNFs}$  take advantage of large interlayer spacing and extremely weakly van der Waals interaction of  $\text{ReS}_2$ , high conductivity and oriented electronic/ionic transport pathway of CNFs, and strong absorption of nitrogen doping to sulfur and polysulfide, thus showing excellent electrochemical performance in LIBs, NIBs, and KIBs. It exhibits reversible capacities of 440 mA h/g after 400 cycles at 100 mA/g in LIBs, 245 mA h/g after 800 cycles at 100 mA/g in NIBs, and 253 mA h/g after 100 cycles at 50 mA/g in KIBs, all of which are much better than that of pure  $\text{ReS}_2$ . Also, we firstly investigate the different electrochemical performance of  $\text{ReS}_2/\text{N-CNFs}$  in LIBs, NIBs, and KIBs. The results will hopefully intrigue more interests in  $\text{ReS}_2$  used on energy storage and conversion.

## Acknowledgments

This work was supported as part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award number DESC0001160. This work was also supported by the National Natural Science Foundation of China (Grant Nos. 51302079), Hunan Provincial Innovation Foundation for Postgraduate (no. CX2016B120). M. Mao's fellowship was supported by China Scholarship Council (grant no. 201606130050).

## Notes

The authors declare no competing financial interest.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2018.01.001>.

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