



Communication

Freestanding carbon encapsulated mesoporous vanadium nitride nanowires enable highly stable sulfur cathodes for lithium-sulfur batteries



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ABSTRACT

Lithium-sulfur (Li-S) battery is one of the most promising energy storage systems due to its large energy density of 2560 Wh kg⁻¹. However, severe shuttle effect of polysulfide intermediates, poor conductivity of S and large volume change during cycling cause fast capacity fading and poor cycle performance. Herein, we demonstrate S nanodots impregnated microporous carbon encapsulated conductive mesoporous vanadium nitride nanowires (S/MVN@C NWs) as high-performance S cathode materials for Li-S batteries. The S nanodots with the size of 2–5 nm are impregnated into the mesopores of MVN@C NWs and further encapsulated with microporous carbon. During cycling, the polysulfides intermediates are strongly chemical anchored by the conductive MVN NWs and further physically trapped by microporous carbon coating within the cathode. The freestanding and binder-free cathode comprising intertwining and interpenetrating S/MVN@C NWs demonstrates highly mechanical flexibility, which deliver a long cycle life of 636 mAh g⁻¹ after 200 cycles at 1 C (1650 mA g⁻¹) and high rate performance with a capacity of 543 mAh g⁻¹ at 10 C. Even at a high areal mass loading of 9.7 mg cm⁻², a large and stable capacity of 7.1 mAh cm⁻² is achieved. The strategy combining microporous carbon coating with high conducting mesoporous metal nitrides opens a feasible route to design large-capacity and high-stability S-based cathodes for Li-S batteries.

1. Introduction

The large demand for portable electronics, electronic vehicles, and intermittent renewable energy sources has spurred the development of advanced energy storage systems and devices [1,2]. Lithium-sulfur (Li-S) batteries are regarded as one of the most promising energy storage systems due to the large theoretical energy density of 2560 Wh kg⁻¹, which is much larger than that of commercial lithium-ion batteries composed of graphite anode and LiCoO₂ cathode. Moreover, sulfur (S) is abundant, low-cost, and environmentally friendly. However, development of Li-S batteries has been hampered by the poor cycling stability, limited S electrochemical utilization and low rate capability mainly due to the poor conductivity of S and its discharge products, severe shuttle effect of soluble lithium polysulfides (Li₂S_n, n = 3–8), and 80% volume expansion of S after full lithiation [3–5]. Many strategies have been explored to design and engineer S-based cathodes to ameliorate the Li storage properties, mainly by improving the conductivity of the electrodes and reducing the shuttle effect of polysulfides. Carbon (C)

materials such as carbon nanotubes, graphene, activated C, and carbon hollow spheres are widely used as S hosts in Li-S batteries due to the large surface area and high conductivity [6–9]. Compared to pure S, S/C composites show improved cycling life by physically confining the Li₂S_n in the pores or carbon host layers [10,11]. However, the weak interaction between non-polar hydrophobic carbon and polar hydrophilic Li₂S_n species undermines the application of carbon in Li-S batteries as polysulfide traps. Recently, polar metal oxides such as SiO₂ [12], TiO₂ [13], Al₂O₃ [14,15], MnO₂ [16], Ti₄O₇ [17] and V₂O₅ [18] as well as metal sulfides including TiS₂ [19], WS₂ [20], and CoS₂ [21] have been proposed as effective polysulfide adsorbents or trappers by utilizing the strong chemical interaction to prolong the cycling life. Nevertheless, most metal oxides and sulfides are not conductive and impede electron transport, resulting in low S utilization and poor rate performance [22–24]. Compared to metal oxides, transitional metal nitrides (TMNs) possess higher electrical conductivity. Very recently, mesoporous TMNs such as VN, TiN, and Mo₂N have been proposed as superior capacitive materials for supercapacitors (SCs) [25–27]. Owing

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to the high conductivity, good structural stability and strong chemical anchoring effect towards Li_2S_n species, TMNs should be promising S host materials in highly stable Li-S batteries. Recently, Goodenough et al. reported mesoporous TiN-S cathode for stable Li-S batteries [28] and Li et al. developed a conductive porous VN nanoribbon/graphene composite for Li-S batteries [29]. Despite the great promise, the drawback of TMNs in advanced Li-S batteries is the small surface area, small pore volume, and open access structure. The large and open accessible mesopores of TMNs cannot efficiently suppress outward diffusion of Li_2S_n , especially with a large S concentration, thus leading to unsatisfactory capacity retention and cycle life. Hence, it is crucial to design and develop high-performance S host materials that not only offer strong anchoring to soluble Li_2S_n species, but also possess high intrinsic electronic conductivity for boasting good Li-S battery performance even at large current densities.

Among TMN candidates, VN is considered as most promising candidates for SCs because it possesses high electrical conductivity ($\sigma_{\text{bulk}} = 1.67 \times 10^6 \Omega^{-1} \text{m}^{-1}$), which are much higher than that of the V_2O_5 [25,29]. Here, conductive mesoporous VN nanowires encapsulated with conductive C (MVN@C NWs) are described as high-performance S host materials for advanced S cathodes of Li-S batteries. The S impregnated MVN@C NWs (S/MVN@C NWs) cathode has the following advantages: (1) the inner mesopores of the MVN core offer nano-scale containers for active S and S nanodots are mainly stitched into the mesopores of VN providing short electron/ion transfer paths; (2) the soluble Li_2S_n intermediates are chemically tethered by mesoporous VN [29] and further physically trapped by the microporous C shell [23], thereby effectively inhibiting outward diffusion and the shuttle effect of soluble Li_2S_n ; (3) the mesopores space of the inner MVN buffers the stress originating from the volume changes of S during charging/discharging processes, resulting in high structure stability of the electrode; (4) VN possesses catalytic properties similar to precious metals thus facilitating the redox reaction kinetics [29]; (5) the conductive and long S/MVN@C NWs are interpenetrated and intertwined together to form a freestanding/binder-free three dimensional (3D) conductive network without a conductive additive or other mechanical supporter, and hence, the paper-like flexible film cathode has a large overall capacity and is suitable for flexible Li-S batteries. With a large S content of 57.2 wt% and areal mass loading of 2.8 mg cm^{-2} , the freestanding and binder-free S/MVN@C NWs cathode delivers a large initial capacity of 1305 mAh g^{-1} at 0.2 C ($1 \text{ C} = 1650 \text{ mA g}^{-1}$), a long cycle life over 200 cycles with a capacity of 636 mAh g^{-1} and a high rate capacity of 543 mAh g^{-1} at 10 C. Moreover, a large and stable areal capacity of 7.1 mAh cm^{-2} is achieved at a high mass loading of 9.7 mg cm^{-2} , offering promising applications in high-energy Li-S batteries.

2. Experimental section

2.1. Preparation of S/MVN@C NWs

2.1.1. Synthesis of V_2O_5 NWs

Firstly, 0.364 g of V_2O_5 powders (99%, Sigma-Aldrich) were mixed with 30 mL of deionized water (DW), followed by adding of 5 mL of H_2O_2 (30%, Sigma-Aldrich) under vigorous stirring. Then, the mixture solution was transferred into a 60 mL Teflon-lined autoclave and kept at 210°C for 72 h. The yellow product of V_2O_5 nanowires was produced via washing with ethanol and DW for several times.

2.1.2. Synthesis of MVN@C NWs

The as-prepared V_2O_5 NWs were dispersed in Tris-HCl buffer (99%, Sigma-Aldrich) solution with the concentration of 10 mM and the pH value of 8.5, then dopamine (DA, Sigma-Aldrich) with the concentration of 1 mg mL^{-1} were added into above solution. After magnetic stirring and polymerization for 30 min, the dark polydopamine coated V_2O_5 nanowires (V_2O_5 @PDA NWs) film were produced by vacuum filtering after washing with DW for three times. The resultant

freestanding film of MVN@C NWs were obtained by further annealing freestanding V_2O_5 @PDA NWs film at 750°C for 3 h under the NH_3 atmosphere. The thickness of MVN@C NWs film can be easily adjusted by changing the mass of MVN@C NWs. For comparison, we synthesized the mesoporous MVN NWs by directly nitriding as-prepared V_2O_5 NWs. The N-doping carbon nanotubes (NCNT) were also fabricated by dissolving MVN@C NWs in 6 M KOH solution to remove the MVN core.

2.1.3. Synthesis of S/MVN@C NWs

A S/carbon disulfide (CS_2) solution was firstly prepared by dissolving S into CS_2 with the concentration of 0.15 g mL^{-1} , and then paper-like MVN@C film ($8 \times 25 \text{ mm}^2$) was soaked into S/ CS_2 mixed solution for 30 min. Subsequently, the film was taken out, put into the glass tube, which was heated at 155°C for 12 h to ensure that the S is fully impregnated into the MVN@C NWs. The S impregnated MVN@C NWs samples with different S mass loading could be obtained by changing the content of sulfur in S/ CS_2 mixed solution. The S impregnated MVN NWs (S/MVN NWs) and the S impregnated NCNT (S/NCNT) were produced in the similar way.

2.2. Polysulfide adsorption test

A polysulfide catholyte was prepared by chemically reacting of sublimed sulfur and lithium sulfide at a molar ratio of 5:1 in an appropriate amount of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1, ratio by volume) by vigorous magnetic stirring at 50°C . Then, equivalent amounts (25 mg) of MVN@C NWs, MVN NWs, and NCNT were immersed into 3 mL of polysulfide catholyte with a concentration of 5 mM for Li_2S_6 , respectively. After stewing for 24 h, digital photos were taken to show the color change of above samples.

2.3. Materials characterization

The morphology and structure of the as-obtained samples were characterized using field-emission scanning electron microscopy (SEM, FEI Nova 450 Nano) and high-resolution transmission electron microscopy (TEM, FEI Titan G2 60-300) equipped with energy-dispersive X-ray spectroscopy (EDX, Oxford). X-ray diffraction (XRD, Philips X' Pert Pro (Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$)), Raman scattering (HR RamLab) and X-ray photoelectron spectroscopy (XPS, ESCALB MK-II) were employed to analyze the structure and component of above samples. The concentration of polysulfide catholyte was evaluated by ultraviolet-visible (UV-Vis, Shimadzu UV-2550). The N_2 adsorption-desorption curves were evaluated using Micromeritics ASAP 2020 analyzer. The average pore distribution were calculated using Barrett-Joyner-Halenda and Density Functional Theory models for mesopores and micropores, respectively. The thermal analysis was performed with Naichi Corporation STA449 in Ar atmosphere at $10^\circ\text{C min}^{-1}$ from room temperature to 600°C . We also measured the conductivity of the film electrodes by four-tip probes method. The conductivity of the VN and MVN@C NWs film electrodes are about 4.3×10^4 and $3.46 \times 10^4 \Omega^{-1} \text{m}^{-1}$. After S impregnation with 57.2% mass loading, S/MVN@C NWs films still exhibits a high conductivity of $2.3 \times 10^4 \Omega^{-1} \text{m}^{-1}$.

2.4. Electrochemical measures

The paper-like binder-free film of the S/MVN@C NWs, S/MVN NWs and S/NCNT were cut into square plate ($4 \times 4 \text{ mm}^2$). The coin-like 2016 type cells were assembled with the above electrodes as the cathode and lithium foil as anode. DOL/DME (1:1, v/v) with 1 M lithium bis (trifluoromethanesulfonyl) and 0.1 M LiNO_3 was used as the electrolyte and Celgard 2300 film as separator. Cyclic voltammogram (CV) profiles were acquired from electrochemical work station (CHI 760e) at the scan rate of 0.1 mV s^{-1} . Galvanostatic discharge-charge tests at different current densities (based on the mass of sulfur) were

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