



Ultrafast synthesis of Te nanorods as cathode materials for lithium-tellurium batteries



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HIGHLIGHTS

- An ultrafast method was applied to prepare tellurium nanorods on nickel foam.
- This Te@Ni materials can be used as cathode without any binders and carbon additives.
- Carbon cloth used as interlayer can further improve the battery performance.

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ABSTRACT

Recently, tellurium has been regarded as a promising cathode material for rechargeable lithium-ion batteries due to its high theoretical volumetric capacity. However, a plethora of research are focusing on impregnating the tellurium into porous carbon materials by the thermal-diffusion method, which would consume large amounts of energy and take prolonged time. Herein, a carbon and binder-free cathode with 100% Te is fabricated by a facile galvanic replacement method on a nickel foam. Driven by the large electrochemical potential difference between Ni and Te, desirable amounts of Te can be obtained in just 10 min with no need of energy input. Li-Te batteries constructed by the as-obtained cathode show relatively good performance in DMSO solvent. To further elevate the performance of this battery especially at low current density, commercial carbon cloth is added between the separator and Te electrode as an interlayer. The cell with interlayer delivers a gravimetric capacity of 116.2 mAh g⁻¹ after 70 cycles at the current density of 100 mA g⁻¹, which is 2.8 times as high as that of a cell without interlayer (40.4 mAh g⁻¹).

1. Introduction

The demand for advanced lithium ion batteries in portable electronics and electric vehicles continues to grow, which boosts a great deal of research efforts in seeking for suitable electrode materials with high capacity, stable cycle performance, and superior rate capability [1–4]. During the past several decades, significant progress has been made to replace the conventional carbon materials in the field of anode materials [5–8]. However, only a handful of improvements has been achieved for the cathode materials [9–13]. In this respect, it is very urgent to find a cathode alternative to address the ever-growing energy demand [14–18].

Among all the alternatives, tellurium has been considered to be a promising candidate due to the following merits [19]. First, the high

density of Te (6.24 g cm⁻³) ensures a high theoretical volumetric capacity (2621 mAh cm⁻³), which is better than values of most other cathode materials and comparable with sulfur (3467 mAh cm⁻³) and selenium (3253 mAh cm⁻³) [20–23]. Second, the electronic conductivity of Te (2.5 S cm⁻¹) is substantially higher than of sulfur (10⁻³⁰ S cm⁻¹) and of selenium (10⁻⁶ S cm⁻¹) which allows for higher active material utilization and better rate capability in a Li-Te battery [24]. More importantly, carbon blacks could be eliminated from the electrode preparation process with such a feature, which would not only save costs, but also make it possible to obtain a 100% Te electrode and therefore improve the capacity calculated for the whole mass of the electrode. For example, it was reported that Zong et al. prepared a flexible carbon-free Te electrode that demonstrated promising potential application as a high performance cathode for Li-Te batteries [25].

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Third, lithium polysulfides and lithium polyselenides are commonly observed in Li-S and Li-Se batteries, which can severely impair the battery performance [26,27]. For Li-Te batteries, the comparable atom size of Te and Li retards the formation of lithium polytelluride, which can mitigate the shuttle effect and enable improved cycling performance [25]. Fourth, the operation of a conventional Li-ion battery corresponds to the Li insertion/extraction reaction, which often induces huge volume changes of electrode materials and finally electrode collapse. But for the Li-Te battery, the discharge product of Li_2Te has been found to be readily dissolved into the DMSO solution, thus avoiding the cathode clogging (usually observed for Li-S batteries due to the formation of insoluble Li_2S) and volume expansion issues [28]. Though the high solubility of Li_2Te would also cause poor stability at low current densities, the use of interlayer (like commercially available carbon cloth) can alleviate this problem.

For now, the study of Li-Te battery is in the very early stage. The finite number of works is mostly focusing on impregnating the tellurium into the porous carbon materials, just like sulfur and selenium. For example, Te molecules confined in a microporous carbon host were reported by Guo et al. and Liu et al. and this material delivered a high volumetric capacity and admirable long-term cyclic stability [24,28]. However, these Te/C composites are inevitably synthesized by the thermal-diffusion method. The high melting point of Te (449.5 °C) means that much energy is consumed. Almost at the same time, Seo et al. synthesized a Te/C composite through the reaction between TeO_2 and C by a new mechanical milling procedure [20]. Apart from the energy-consumption, unfortunately, this method is also time-consuming. Therefore, a time-saving and energy-efficient method to prepare Te electrodes is highly desirable.

In this work, we demonstrate the galvanic replacement method as an ultrafast, cost-effective, and energy-efficient approach to prepare Te cathodes for Li-Te batteries. Homogeneous Te nanorods on the flexible 3D Ni foam electrode (denoted as Te@Ni) can be obtained at room temperature within just 10 min by utilizing the large equilibrium potential difference between HTeO_2^+ and Ni, thus enabling a possibility to synthesize Te@Ni electrode on a large scale [29–31]. Meanwhile, the as-prepared Te@Ni electrode can be directly used as cathode without any binders and carbon additives in assembling Li-Te batteries, which would further save manufacturing time and cost of batteries. Remarkably, this binder-free electrode shows a much higher gravimetric capacity and better cyclability in electrolyte of 1 M lithium perchlorate (LiClO_4) in dimethyl sulfoxide (DMSO) than those in two other electrolytes, such as 1 M lithium hexafluorophosphate (LiPF_6) in a mixed solvent of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) and 1 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in dimethoxyethane (DME) and 1,3-dioxolane (DOL). Furthermore, it has been found that insertion of commercial carbon cloth between the separator and Te@Ni electrode as an interlayer can further improve the cell performance.

2. Experimental section

2.1. Preparation of Te@Ni electrode

In a typical process, 0.135 g of Na_2TeO_3 (Aladdin) was dissolved in 60 mL of deionized water (18.2 M Ω cm, produced by a Millipore-Q purification system) under vigorous stirring for 10 min. Subsequently, 2 mL of 3 M HCl aqueous solution (Shanghai Chemical Reagent Co., Ltd.) was slowly dropped into the solution. During this process, white precipitates of H_2TeO_3 were formed at the beginning and then turned to HTeO_2^+ with further addition of HCl solution, which can be readily dissolved in water [29]. For the next step, 10 mL of the as-prepared solution was transferred into a small bottle (volume: 25 mL). A piece of nickel foam (diameter: 12 mm; thickness: 1 mm; area density: 300 g m $^{-2}$), which was ultrasonically cleaned by 3 M HCl, deionized water, and alcohol (Shanghai Chemical Reagent Co., Ltd.) for 15 min in

sequence, was put into the bottle. After holding the reaction at 25 °C for 10 min, the as-obtained Te@Ni material was taken out and rinsed with alcohol several times, which was finally dried at 40 °C in a vacuum oven.

2.2. Instruments and measurements

Field emission scanning electron microscopy (FESEM) images and energy-dispersive spectroscopy (EDS) were collected on a Nova NanoSEM 450 (FEI Company The Netherlands). Transmission electron microscopy (TEM) pictures were captured on an FEI Tecnai G2 F30. X-ray diffraction (XRD) patterns were recorded by an X'pert PRO diffractometer (PANalytical B.V.) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) as the X-ray source operating at 40.0 kV and 40.0 mA within the 2θ range from 10° to 80°. Raman spectra were collected using a LabRAM HR800 Raman spectrometer (Horiba JobinYvon Co.) with an excitation wavelength of 532 nm. UV-vis absorption spectra were collected on a SHIMADZU UV-3600 UV-vis spectrometer.

2.3. Electrochemical measurements

The 2032-type coin cells were assembled in a glove box filled with Ar and the glass fiber (diameter: 16 mm, whatman, GF/B) was used as separator and metallic lithium foil (diameter: 15 mm) as counter electrode. The as-synthesized Te@Ni was directly used as working electrode without any further treatment. The Te has been found to be remarkably soluble in binary mixtures of thiols and ethylenediamine, so the mass loading of Te in Te@Ni composite can be easily calculated by subtracting the weight of Ni [32]. To reduce the errors, 30 pieces of Te@Ni samples were measured and the average mass loading of Te is about 0.4 mg. The average mass of Ni can also be measured through this process, which is about 33.6 mg. Therefore, the ratio of Te to Ni by volume and by weight is 1:59 and 1:84, respectively. Commercial carbon cloth obtained from Shanghai Hesen Electric Co., Ltd. (thickness: 0.35 mm; mass: 160 g m $^{-2}$; porosity: 75%; diameter: 15 mm), which was ultrasonically cleaned with ethanol and water for 15 min, respectively, was placed between the separator and Te@Ni electrode. The electrolyte was a solution of 1 M lithium perchlorate dissolved in DMSO solution. Galvanostatic charge and discharge were recorded on a Land Battery Measurement System (Land, China) in the voltage range of 1.7–2.6 V versus Li^+/Li at the temperature of 25 °C. Cyclic voltammetry (CV) curves were obtained at a scan rate of 0.2 mV s $^{-1}$ on a CHI750D potentiostat (Chenhua Co. Shanghai). Two other electrolytes used are: (1) 1 M lithium hexafluorophosphate (LiPF_6) in a mixture solvent of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (v/v, 1:1:1); (2) 1 M LiTFSI in dimethoxyethane (DME) and 1,3-dioxolane (DOL) (v/v, 1:1).

3. Results and discussion

Fig. 1a illustrates the schematic preparation of Te nanorods deposited onto the three-dimensional network of nickel foam (abbreviated as Te@Ni) via a facile galvanic replacement reaction. After immersing the Ni foam into an acidic solution containing HTeO_2^+ ions, the elemental Te would be quickly formed. At the same time, Ni foam was oxidized to Ni^{2+} ions and then released into the solution [33]. The existence of Ni^{2+} in the solution can be proved by the UV-vis spectrum (Fig. S1). It has to be noted that this galvanic replacement reaction must be carried out in acidic solution. In theory, the formation of Te@Ni can also happen in alkaline media because half cell reaction 2 (seen at the end of this paragraph) has a more positive equilibrium potential than half cell reaction 1 under such a condition. However, when the Ni foam was put into the Na_2TeO_3 solution (pH = 10.6), no noticeable change of Ni foam had been observed even after 48 h at 25 °C (Fig. S2), which may be ascribed to the variation of redox potential value depending on the actual conditions or kinetic barrier on surfaces. In acidic solution,

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