



Nanostructured titanium nitride as a novel cathode for high performance lithium/dissolved polysulfide batteries



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HIGHLIGHTS

- Titanium Nitride (TiN) as a novel cathode material for lithium sulfur batteries is prepared.
- The effect of polysulfide concentration on the new cathode material is investigated.
- The effect of cut off voltage on the new cathode material is investigated.
- TiN electrode exhibits remarkably enhanced discharge capacity and capacity retention.
- The mechanism for enhancement of electrochemical performance of Li₂S was investigated.

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ABSTRACT

Lithium–sulfur (Li–S) batteries could potentially revolutionize the rechargeable battery market due to their high energy density and low cost. However, low active material utilization, electrode volumetric expansion and a high rate of capacity fade due to the dissolution of lithium polysulfide intermediates in the liquid electrolyte are the main challenges facing further Li–S battery development. Here, we enhanced Li–S batteries active material utilization and decreased the volumetric expansion by using the lithium/dissolved polysulfide configuration. Moreover, a novel class of cathode materials, Titanium Nitride (TiN), was developed for polysulfide conversion reactions. The surface chemical environment of the TiN has been investigated by X-ray photoelectron spectroscopy (XPS) analysis. The existence of S–Ti–N bonding at the cathode electrode surface was observed, which indicates the strong interactions between TiN and polysulfides. Therefore, the TiN electrode retains the sulfur species on the cathode surface, minimizing the active material and surface area loss and consequently, improves the capacity retention. The resultant cells demonstrated a high initial capacity of 1524 mAh g⁻¹ and a good capacity retention for 100 cycles at a C/10 current rate.

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1. Introduction

Advances in portable electronic devices and electric vehicles require efficient electrical energy storage systems, such as rechargeable batteries with high energy density and long lasting cycle performance. Among the most promising energy storage systems, lithium–sulfur (Li–S) batteries could significantly improve the rechargeable battery market due to their high energy density of 2,600 W h kg⁻¹ and theoretical capacity of 1675 mAh g⁻¹ [1]. In addition, sulfur is environmentally friendly and has a low cost [1–3]. However, there are some challenges facing Li–S battery

development, such as: low active material utilization, high self-discharge products, volumetric expansion associated with intermediate products, and high rate of capacity fade due to the dissolution of lithium polysulfide intermediates in liquid electrolyte, which also increase the redox shuttle reactions and lithium corrosion [1,3,4]. In order to overcome these obstacles, many studies have attempted to develop various cathode materials such as functionalized carbon materials, graphene oxides, and conducting polymers with high surface area and porosity [4–9]. These materials were designed to enhance Li–S cell capacity retention due to their ability to maintain polysulfides by physisorption, or to chemisorb lithium polysulfides because of their hydrophilic nature [10,11]. Metal oxides, such as TiO₂, Al₂O₃ and SiO₂ as well as metal sulfides, such as TiS₂ and ZrS₂ were also reported to adsorb lithium polysulfides and reduce redox shuttle reactions in Li–S batteries

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[12–16]. In addition, Ti_4O_7 has been demonstrated to enhance the redox chemistry and cyclability due to its sulfiphilic surface and good electron conductivity [17].

On the other hand, a dissolved polysulfides configuration has been reported to have high reaction activity and sulfur utilization compared to conventional Li–S batteries [18–20]. Barchasz et al. demonstrated that the discharge capacity could be increased to up to 1400 mAh g^{-1} at a low rate of C/100, using carbon foam and dissolved 0.5 mol L^{-1} Li_2S_6 – Li_2S_8 catholyte. However, its capacity decreases to 1200 mAh g^{-1} within 10 cycles [21]. Demir–Cakan et al. showed the capacity performance of Li_2S_5 with a Ketjen Black carbon cathode at C/10 rate. Their results show an almost 1200 to 500 mAh g^{-1} capacity, and 500 to 300 mAh g^{-1} capacity deactivation for 0.3 and $0.1 \text{ M Li}_2\text{S}_5$ catholyte concentrations, respectively, within 70 cycles [22]. The low performance of carbon materials is mainly due to their poor adsorption properties toward lithium polysulfides. Therefore, in order to take full advantage of dissolved polysulfide Li–S battery, it is important to enhance its capacity retention and cycle lifetime using efficient cathode materials. The studies that emerged from the reported works indicate that the battery performances centered mainly on the development of cathode materials.

Based on our experiences in improving the battery performances using nanostructured electrodes [20,23,24], we investigated transition metal nitrides as a new class of cathode materials and demonstrated the superior performance in a Li/dissolved polysulfide battery configuration for the first time. Transition metal nitrides are well known materials for supercapacitors and lithium-ion batteries due to their high reversible insertion and extraction of ionic species and the capability of storing lithium by the intercalation mechanism [25–30]. Different types of metal nitride such as TiN [31], VN [32], Mo_2N [33,34], Zn_3N_2 [35], Ni_3N [36], NbN [37], have been demonstrated as efficient electrode materials for lithium-ion batteries and supercapacitors. Among the metal nitrides, titanium nitride (TiN) has unique properties such as high electrical conductivity (4000 – $55,500 \text{ S cm}^{-1}$) [37] and thermodynamic stability and corrosion resistance due to the presence of a triple covalent bond between titanium and nitrogen. In this work, titanium nitride (TiN) is investigated as a novel cathode material for Li/dissolved polysulfide batteries since it can adsorb lithium polysulfides effectively and transfer electrons in a facile manner. As revealed by X-ray photoelectron spectroscopy (XPS) analysis, sulfur interacts with TiN nanoparticles during the discharge process, and resulted in S–Ti–N, which retains the sulfur species on the cathode surface. The adsorbed higher order polysulfide species undergo reduction to lower order polysulfides by transfer of electrons from the TiN electrode. As a result, the active material and surface area loss were reduced and the capacity and capacity retention of the cell were enhanced.

2. Experimental details

2.1. Preparation of titanium nitride

Titanium oxide powder (TiO_2 , 10 – 25 nm size, US Research Nanomaterials) was used as precursor. The powder was first loaded into a zirconia boat and placed in a tubular reactor, which was connected to the gas feed system. Initially, the reactor was purged using 150 mL/min Argon (Ar) gas for 1 h ; followed by 200 mL min^{-1} pure NH_3 gas for 30 min to stabilize the gas flow. The reactor was then heated to $250 \text{ }^\circ\text{C}$, in 8 h , held for 40 min , then raised to $1000 \text{ }^\circ\text{C}$ over 3 h and maintained for 1 h . The furnace cooled down to room temperature followed by flowing 150 mL min^{-1} Ar gas overnight.

2.2. Fabrication of electrodes and cell assembly

The cathode slurry was prepared by adding 10 wt\% of Poly (vinylidene fluoride) PVDF, as binder and *N*-methyl pyrrolidinone (NMP) as solvent to the cathode materials (TiN). The slurry was then coated on aluminum (Al) foil (0.1 mm thick) and dried at $80 \text{ }^\circ\text{C}$ under vacuum for 12 h .

Elemental sulfur S_8 , lithium sulfide Li_2S , Bis(trifluoromethane) sulfonimide lithium salt $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSI, triethylene glycol dimethyl ether (TG_3), were purchased from Aldrich and used as received. Catholyte solutions with 0.2 , 0.6 , $0.8 \text{ M Li}_2\text{S}_8$, 0.1 M LiTFSI , and 1 M LiNO_3 were prepared by stirring appropriate amounts of S_8 and Li_2S into TG_3 at $70 \text{ }^\circ\text{C}$ for 8 h . $8 \text{ } \mu\text{L}$ of catholyte solution was added on the positive electrodes with 7 mg cm^{-2} electrode loading. Coin cells (CR2032) were assembled using polypropylene separator (Celgard 2400) and lithium foil anode inside the Ar-filled glove box.

2.3. Characterization and electrochemical measurements

The phase purity of the cathode electrode materials was characterized using a Rigaku Miniflex 600 X-Ray Diffractometer. Cathode material morphology was characterized with field emission scanning electron microscopy (JEOL 7600F, FESEM). The specific surface areas of the electrode materials were measured by Braunauer-Emmet-Teller (BET) multimolecular adsorption method (Micromeritics Tristar II surface area/porosimeter). Galvanostatic discharge-charge tests were conducted using a Maccor Model 4200 Automated Test System between the voltage range of 1.5 – 3 V and 1.8 – 3 V (vs. Li/Li^+) at room temperature. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) measurements were applied using a Gamry potentiostat reference 3000. The voltammetry was performed at a scan rate of 0.05 mV s^{-1} , and a voltage range of 3 to 1.5 V (vs. Li/Li^+). EIS were recorded between 1 MHz and 0.1 Hz , and AC amplitude of 10 mV at room temperature.

3. Results and discussion

3.1. Structure and morphology

Nanostructured TiN was prepared by heating titanium oxide (TiO_2) under an ammonia atmosphere. Crystal structure of the prepared TiN analyzed by X-ray diffraction (XRD) (Fig. 1a) presents five diffraction peaks of TiN (111), (200), (220), (311) and (222). The positions and intensities of TiN diffraction peaks can be indexed to the face-centered cubic phase structure of TiN (JCPDS file no. 38-1420) with lattice constant $a = 0.424 \text{ nm}$ (Fig. 1b). Crystallite size was calculated to be 16 nm from broadening of the diffraction peak using Scherrer's equation [38].

Scanning electron microscopic (SEM) image depicted agglomeration of TiN nanoparticles (Fig. 1c). Transmission electron microscopic (TEM) image showed the connectivity between irregular shaped grains, imparting electronic conductivity (Fig. 1d). Average particle size was found to be 30 nm from the measurement of about 100 particles found in an arbitrarily chosen area of the enlarged microscopic images. Selected area electron diffraction (SAED) pattern further confirmed the polycrystalline nature of the sample (Fig. 1e). The d-spacing from inner to outer can be indexed to the (111), (200), (220), (311) and (222) planes of a cubic phase, which is in a good agreement with the XRD results. The BET surface area of TiN was measured to be $22.1 \text{ m}^2 \text{ g}^{-1}$ using BET sorptometry.

3.2. Electrochemical performance

The electrochemical performance of the TiN cathode at a 0.1 C rate was examined with an Al foil without TiN coating, and TiN

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