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Highly catalytic and stabilized titanium nitride nanowire array-decorated graphite felt electrodes for all vanadium redox flow batteries

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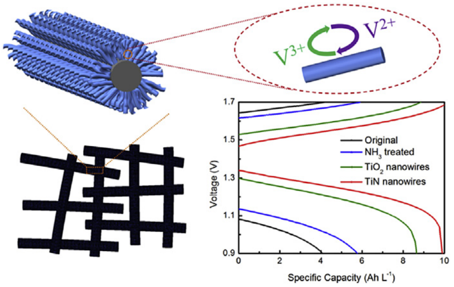
HIGHLIGHTS

- Propose a binder-free TiN nanowire array-decorated electrode for VRFBs.
- Energy efficiency is up to 77.4% at 300 mA cm^{-2}, enhancing more than 15%.
- Electrolyte utilization is up to 73.9% at 300 mA cm^{-2}, enhancing more than 43%.
- High stability and capacity retention are achieved by present battery.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we prepare a highly catalytic and stabilized titanium nitride (TiN) nanowire array-decorated graphite felt electrode for all vanadium redox flow batteries (VRFBs). Free-standing TiN nanowires are synthesized by a two-step process, in which TiO_2 nanowires are first grown onto the surface of graphite felt via a seed-assisted hydrothermal method and then converted to TiN through nitridation reaction. When applied to VRFBs, the prepared electrode enables the electrolyte utilization and energy efficiency to be 73.9% and 77.4% at a high current density of 300 mA cm^{-2}, which are correspondingly 43.3% and 15.4% higher than that of battery assembled with a pristine electrode. More impressively, the present battery exhibits good stability and high capacity retention during the cycle test. The superior performance is ascribed to the significant improvement in the electrochemical kinetics and enlarged active sites toward V^{3+}/V^{2+} redox reaction.

1. Introduction

With increasingly pressing concerns over environmental issues and energy sustainability due to the consumption of fossil fuels, there has been a global agreement that renewable energies such as solar and wind are essential to economic and social development [1–3]. However, the fluctuant and intermittent nature of electricity generated from these renewables makes them less appealing for practical applications [4,5]. Underlying these considerations, the large-scale energy storage technology such as redox flow battery, offering well-established ability to improve grid reliability and utilization with inherent safety, moderate cost, ease of scalability and flexible operation, is an effective method to address this matter [6,7]. Particularly, the vanadium redox flow battery (VRFB) attracts the most attentions, owing to its advantages of significantly low

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cross-contamination and long service life by employing the same element, vanadium, in both positive and negative electrolytes [8,9].

VRFBs store and release electrical energy through electrochemical reactions of the VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox species in the aqueous electrolyte. As a core component of the battery, the electrode provides electroactive surfaces and conducts electrons for redox reactions to take place [10]. Battery polarization, including the activation, ohmic and concentration losses are strongly dependent on the electrode and its surface chemistry [11]. In particular, the activation loss, which is plagued by the poor kinetic reversibility and electrochemical activity towards the vanadium redox reactions, has been a long-term barrier to improve the battery performance during the battery operation [12], often limiting the system to an operating current density lower than 100 mA cm^{-2} [13]. Thus, minimizing the polarization to endow the VRFBs with high energy efficiency at elevated operating current densities, best expressed as high power density, is always desired [14,15]. At the cell level, the augment of power density is effective for decreasing the size of the power stack, including the total area of bipolar plates, electrodes and membranes which represent a significant expense of the battery system [16].

Possessing wide operating potential range, satisfactory chemical and mechanical stability and availability with high electrical conductivity at low cost, carbonaceous materials such as graphite felts have been extensively used as electrodes in the past few decades [17]. Even though carbonaceous electrodes themselves already inherently possess catalytic effects towards vanadium species reactions, the optimization of electrode material is still a necessity to enhance the kinetics of the redox reactions [18]. To date, various surface modification approaches including the acid, thermal and nitrogen treatments have been introduced. While these techniques have been proved to create more active sites for vanadium redox reactions, excessive surface oxidation of carbon material leads to electrode corrosion and eventual disintegration [19]. An alternative approach to increase the active sites is to introduce nanostructured electrocatalysts on the surface of the electrode [20]. To date, a variety of metal-based (metal and metal oxide) and carbon-based materials (carbon nanotube, graphene, and carbon nanoparticles) with high electronic conductivities and specific surface areas have been reported in the literature [21–23]. The performance enhancement varies depending on the distribution uniformity and preparation process of the nanostructured electrocatalysts. High cost of noble metal catalysts as well as tedious synthesis procedures limited their practical application in VRFBs to some extent [24].

In recent years, transition metal carbides, nitrides and carbonitrides have been attracted increasing attention due to their remarkable properties such as high melting point, exceptional chemical stability, and high hardness [25]. Conductivity and catalytic activity of these types of catalysts are also comparable to those of metals [26]. In a recent publication, Wei et al. [27] and Yang et al. [28] performed pioneering work in applying TiC and TiN nanoparticles in aqueous media for catalyzing V^{3+}/V^{2+} redox reaction for VRFBs, respectively. These titanium carbide and nitride nanoparticles were employed to decorate on the surface of carbon fibers via binders to enhance the electrochemical activity of electrodes, enabling a high current-density operation.

In the present work, we propose the use of inexpensive and conductive TiN nanowires as catalysts to enhance the electrochemical activity of the graphite felt. Free-standing TiN nanowires were grown on the surface of graphite felt by a two-step process as illustrated in Fig. 1. TiO_2 nanowires were first grown onto the graphite felt via a seed-assisted hydrothermal method. The samples were subsequently thermally annealed in ammonia gas at a temperature above 700 °C, to convert them to TiN. When applied to flow batteries, the proposed electrode significantly improved the energy efficiency (the ratio of energy between the discharge and charge processes) of a VRFB by enhancing the kinetics of the sluggish V^{3+}/V^{2+} redox reaction, especially under high-power-density operation. In addition, it is demonstrated that the present battery exhibits a significantly improved rate capability and capacity retention during the cycle tests, in comparison to that of a pristine electrode. These superior results suggest that stabilized metal nitride nanomaterials could open up new avenues for the fabrication and application of high-performance electrodes for VRFBs. Fundamental understanding of the catalyst mechanism causing the improvement of battery performance was further discussed.

2. Experimental

2.1. Cyclic voltammetry and electrochemical impedance spectra

Cyclic voltammetry (CV) tests were obtained on a workstation (Autolab, PGSTAT30). A conventional three-electrode electrochemical cell was established with a glassy carbon electrode (GCE) with an area of 0.283 cm^2 as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum mesh as the counter electrode. The GCE was modified by depositing different catalysts onto it and served as the working electrode as reported elsewhere [27]. 10 mg of commercialized TiN nanoparticles (Aldrich), Vulcan XC-72 carbon nanoparticles (E-TEK) with similar particle size were compared to identify the electrochemical activity of the TiN. These nanoparticles were separately dispersed to 1.9 mL ethanol, to which 0.1 mL of 5 wt% Nafion emulsion was added. After 50 min of sonication, a uniform suspension was achieved and 30 μL of the ink was pipetted on top of the GCE and dried in air. The measurement was performed at −0.7 V to 0 V (vs. SCE) in a solution containing 0.1 M VO^{2+} + 3 M H_2SO_4.

To further determine the rate determining step of the electrode reaction on the graphite felt electrode in this work, an electrochemical impedance spectra (EIS) test was performed with a potentiostat (EG&G Princeton, model 2273). A typical three-electrode system, in which the SGL graphite felt, a platinum mesh, and a saturated calomel electrode (SCE) were employed as the working electrode, counter electrode, and a reference electrode, respectively.

2.2. Fabrication of TiN nanowire decorated electrode

Binder-free TiN nanowires were directly grown on the surface of graphite felt via a two-step process. First, TiO_2 nanowires were grown on the graphite felt using a hydrothermal method as previously reported [29,30]: Graphite felt (SGL company, GFA series, 18 mm × 26 mm) was cleaned with ethanol and dried at 60 °C. Then, the graphite felt was immersed into a 0.2 M $TiCl_4$ aqueous solution (achieved by dissolving 1.10 mL $TiCl_4$ into 48.90 mL concentrated hydrochloric acid) for 30 min and dried in ambient air at room temperature for 10 h, forming the TiO_2 seeds on the surface of the graphite felt. 18.75 mL of concentrated hydrochloric acid, was added into 18.75 mL deionized water, and then mixed with 0.56 mL titanium n-butoxide. This solution, along with the TiO_2 seed coated graphite felt, was transferred to a Teflon-lined stainless autoclave (50 mL volume). The hydrothermal reaction was maintained at a constant temperature of 150 °C for 5.0 h in an electric oven and then cooled at room temperature. The sample was then sonicated with DI water for 5 min and dried at ambient air. This process uniformly covered the entire surface of the carbon fibers by a white film of TiO_2 nanowires. To convert TiO_2 to TiN, the samples were annealed in NH_3 at temperatures of 700, 800, and 900 °C for 1.5 h with a heating rate of 2 °C min^{-1}, respectively. The color of the