

Vanadium Oxides

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Vanadium-based compounds exhibit a range of oxidation states, including V⁵⁺, V⁴⁺, V³⁺, and V²⁺, making them feasible to composite with many other anions and cations to form vanadium oxides, vanadium carbides, vanadium nitrides, vanadium sulphides, vanadium phosphates, and metal vanadates. Among them, vanadium oxides have attracted interest for energy storage in the past decades.

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1. Introduction

Vanadium-based compounds exhibit a range of oxidation states, including V⁵⁺, V⁴⁺, V³⁺, and V²⁺, making them feasible to composite with many other anions and cations to form vanadium oxides, vanadium carbides, vanadium nitrides, vanadium sulphides, vanadium phosphates, and metal vanadates. Among them, vanadium oxides have attracted interest for energy storage in the past decades. Due to the distortion of V-O coordination polyhedral and the conversion of diverse oxidation states, vanadium oxide compounds present higher specific capacity compared with the other vanadium-based materials when they are used as electrodes [1]. The most common phases are orthorhombic V₂O₅, bilayered V₂O₅·nH₂O, VO₂, V₃O₇·H₂O, V₆O₁₃, and V₂O₃. Orthorhombic V₂O₅ and bilayered V₂O₅·nH₂O possess layered structures with open ion diffusion channels between layers [2], strengthening the electrochemical performance. Nevertheless, they show low stability in aqueous electrolytes, poor conductivity, and a low ionic diffusion coefficient, which consequently results in poor long-term cycling performance. In the following sections, the general strategies undertaken to improve the cathode performance are indicated, and the structure–performance relationship as reported in the last five years is discussed.

2. Approaches to Improve the Electrochemical Performance of V₂O₅

2.1. Nanostructure Engineering

Nanostructure engineering is a promising approach to enhance the electrochemical performance of cathode materials, dealing with all aspects of design and structures on the nanoscale. Nanostructured electrode materials (tens of nanometers) offer large surface area, more active sites, and short electron/ion transport paths, which is beneficial to accelerate reaction kinetics enabling high rate capability. The nano-sized hollow structure cannot only alleviate the structural stress upon cycling, but it can also provide shortened ion and electron transport paths, and enhance the surface capacitive behavior. V₂O₅ nanospheres with a diameter of about 450 nm and shell thickness of 50 nm delivered ultrahigh reversible capacity (327 mAh g⁻¹ at 0.1 A g⁻¹), and excellent rate (146 mAh g⁻¹ at 20 A g⁻¹) and cycling behavior (147 mAh g⁻¹ after 6000 cycles at 10 A g⁻¹; 122 mAh g⁻¹ after 10,000 cycles at 15 A g⁻¹), indicating superior performance as compared with commercial V₂O₅, when applied for aqueous zinc ion batteries [3]. In contrast with aqueous zinc ion batteries, there are more recent reports on aqueous lithium ion batteries (i.e., mesoporous nanoflowers [4] and triple hollow shell [5] V₂O₅ structures), giving motivation to researchers to work more intensively on multivalent systems.

2.2. Structural Stability Enhancement

The cycling stability of the cathode is affected by irreversible phase changes due to structural degradation. It has been proved that preintercalation of guest species such as Li ions, water molecules, and organic molecules can stabilize the host structure and enhance the ions' diffusion [5][6]. In particular, Li_xV₂O₅·nH₂O had a larger spacing of 13.77 Å and higher diffusion coefficient of Zn²⁺ than in V₂O₅·nH₂O [7]. In that case, the enlarged layer spacing and fast Zn²⁺ diffusion favors the rate capacity and cycling performance, reaching 192 mAh g⁻¹ after 1000 cycles at 10 A g⁻¹.

2.3. Surface Coating

The surface coating acts as a protective layer on the electrode surface, which can prevent volume changes and suppress the dissolution of active materials. In that case, graphene is a promising candidate to improve the electronic conductivity and inhibit dissolution. The exceptional conductivity, abundant adsorption sites, and short diffusion paths are expected to enhance the transport processes within the oxide nanomaterials. A major advantage of graphene over other carbon materials, such as graphite and carbon nanotubes, is the presence of oxygen-containing groups on the edges and surfaces, which strongly influence the size, shape, and distribution of metal oxide nanostructures on graphene.

2.4. Formation of Solid Electrolyte Interface Film

Solid electrolyte interface (SEI) has been proved to effectively prevent the dissolution of electrode materials [8]. For instance, Zhou et al. discovered that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ protects manganese from dissolution in the case of Ca_2MnO_4 , decreases impedance, lowers activation energy, and facilitates the intercalation/deintercalation of zinc ions without fluctuations of discharge capacity after 1000 cycles at 1 A g^{-1} [9]. This approach could also be applied for V_2O_5 cathode.

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