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Electrochromic thin films of sodium intercalated vanadium(V) oxide xerogels: Chemical bath deposition and characterization

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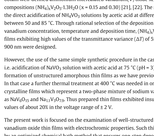
Highlights

- Optimized chemical bath method is designed for $Na_{0.33}V_2O_5{\cdot}nH_2O$ thin films.
- Well-structured layered thin films with nanosized morphology.
- Transmittance variance of 55% is reproducible up to 500 cycles.
- 3-year aging does not affect the electrochromic properties of the thin films.

Abstract

An optimized chemical bath method is applied to obtain well-structured thin films with composition $Na_{0.33}V_2O_5{\cdot}nH_2O$ ($1 < n < 1.8$ and 1.3). The method is based on a controlled precipitation reaction that takes place in the system of sodium metavanadate and diethyl sulfate at 85 °C. The film structure, morphology and the changes occurring during prolonged aging are examined by XRD, IR spectroscopy, TG-DTA, SEM and AFM. The electrochemical and electrochromic properties are studied by cyclic voltammetry and UV–vis spectroscopy. The as-deposited thin films are characterized with high optical transmittance varying between 40 and 70% at the 500 nm visible region in dependence on film thickness. The $Na_{0.33}V_2O_5{\cdot}nH_2O$ thin films exhibit stable electrochemical cycling combined with relatively high electrochromic activity. The reproducibility of the transmittance variance of 55% after 500 cycles in the electrochromic cell is a promising result for the potential application of $Na_{0.33}V_2O_5{\cdot}nH_2O$ thin films in electrochromic devices.

Graphical abstract



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Introduction

Vanadium(V) oxide and derived compounds have been extensively studied due to valuable chemical and physical properties which determine a wide range of applications in catalysis, high-energy lithium batteries and a variety of electric and optical devices. The synthetic procedures at ambient conditions usually produce hydrated vanadium(V) oxides, $V_2O_5{\cdot}nH_2O$, known as xerogels which adopt layered structures with V_2O_5 layers and interstitial water molecules [1,2]. Vanadium(V) oxide xerogels like crystalline V_2O_5 are typical intercalation compounds with multiple valence state of vanadium which enables redox-dependent properties [3–5]. Due to the high intercalation capacity (for instance, a lithium intercalation capacity about 1.4 times larger than that of crystalline V_2O_5) [1] they have a potential for application like rechargeable cathodes for lithium batteries [8]; [9], micro-batteries [6], supercapacitors [10], electrodes [11] and humidity sensors [12]. The reversible cation intercalation/deintercalation within the layered framework is concomitant with reversible reduction/oxidation of V(V) to V(IV) or to a lower valence vanadium state giving rise to easy color changes: yellow (V(V)), blue (V(IV), green (V(III) or a mixture of V(V) and V(IV)) and violet (V(II)) [2]; [6]. The multi-colored electrochromism demonstrated by $V_2O_5{\cdot}nH_2O$ xerogels makes them very attractive since it provides the opportunity to extend the range of hues of the electrochromic materials. Vanadium(V) oxide xerogels under the form of thin films on electroconductive glass substrates have been used in electrochromic devices [13]; [14]; electrochromic mirrors [14], "smart windows" designed for architectural purposes to control light transmittance [15]; [16]; [17] and controlled reflectance mirrors for vehicles [18].

The thin film properties, including $V_2O_5{\cdot}nH_2O$ xerogels, are well known to depend essentially on its microscopic characteristics [19]; [20] such as structure, crystallinity and morphology, which can be governed by the deposition method and the deposition parameters (kind and concentration of the precursors, rate of deposition, temperature, pressure, etc.). Therefore, the choice of the valid synthetic procedure is a powerful tool for control and optimization of the material properties.

In this regard, we have recently developed a simple chemical bath deposition method to obtain well-defined ammonium intercalated vanadium(V) oxide xerogel with the compositions $(NH_4)_xV_2O_5{\cdot}3.3H_2O$ ($x = 0.15$ and 0.30) [21; 22]. The method is based on the direct acidification of NH_4VO_3 solutions by acetic acid at different temperatures between 50 and 85 °C. Through rational selection of the deposition parameters like temperature, time of deposition and deposition time, $(NH_4)_xV_2O_5{\cdot}1.3H_2O$ thin films exhibiting high values of the transmittance variance (ΔT of 55% at 400 and 900 nm were designed.

The present work is focused on the examination of well-structured hydrated sodium vanadium oxide thin films with electrochromic properties. Such thin films are prepared by an optimized chemical bath method that ensures one-step deposition of the thin films at low temperature. For the purpose we have applied a different synthetic approach: instead of a direct acidification, we have used here an indirect acidification through the hydrolysis of diethyl sulfate present in the chemical bath. This controlled precipitation reaction gives rise to the deposition of thin films of vanadium(V) oxide xerogel with composition of $Na_{0.33}V_2O_5{\cdot}nH_2O$ having well-organized structure and nanosize in the nano-scale region. These thin film characteristics are advantageous to achieving electrochemical stability and high ΔT value of 55% which is reproducible for 500 cycles. The changes during the film aging are studied in respect to the film structure, V(V) reduction and electrochromic effect.

It is worth emphasizing that the as-prepared well-structured $Na_{0.33}V_2O_5{\cdot}nH_2O$ composition (solid or film) is highly beneficial for further obtaining a variety of chemical compositions. Thus, once obtained it can be used to produce either lower hydrated xerogels $Na_{0.33}V_2O_5{\cdot}nH_2O$ ($0.3 < n < 1$) or a single phase of NaV_2O_5 by thermal treatment at an appropriate temperature. All these compositions having a layered or tunnel structure can serve as host matrices for intercalation processes which open opportunities for different applications. From this point of view the difference with the previously studied $(NH_4)_xV_2O_5{\cdot}1.3H_2O$ compositions is obvious: their thermal treatment produces the well studied V_2O_5.

Section snippets

Material and methods

Thin film deposition is performed onto commercially available glass substrates. They are coated with a conductive, transparent thin layer of SnO_2:F (FTO) with 80% optical transparency in the visible spectrum and electrical resistance of 10–20 Ω/cm². Before deposition, the substrates were cut into pieces with the dimensions 40 mm × 25 mm × 2 mm and cleaned in the following order: with detergent, alkaline solution, 1:1 diluted hydrochloric acid, hexane, acetone and rinsed with deionized water and dried...

Characterization of the thin films

The composition and structure of both thin films and precipitate from the chemical bath were examined using a Rigaku Ultima IV X-ray diffractometer with CuKα radiation. The thermal studies (TG and DTA) were carried by a LABSYS™ Evo apparatus (SETARAM) in a temperature interval of up to 500 °C in an airflow at a heating rate of 10 °C/min. Infrared spectra were recorded with a Perkin-Elmer System 2000 infrared interferometer using KBr disks.

The morphology of the thin films was observed by scanning...

Chemical consideration for film formation

The chemistry of the deposition process is based on a controlled precipitation reaction resulting from the acidification of the $NaVO_3$ solution that occurs in the presence of diethyl sulfate. The main idea for the precipitation process was taken from a previous study of one of the authors [24]. Above 65 °C the hydrolysis of diethyl sulfate takes place according to the reaction:

$$(CH_3CH_2O)_2SO_2(aq) + 4H_2O(l) \rightarrow 2CH_3CH_2OH(aq) + 2H_3O^+(aq) + SO_4^{2-}(aq).$$

The concentration of H_3O^+ gradually increases (decreasing pH to about...

Conclusions

Well-structured nano-sized thin films with compositions $Na_{0.33}V_2O_5{\cdot}nH_2O$ ($n = 1$ and 1.3) are successfully deposited by an optimized chemical bath method where the acidification of $NaVO_3$ solution occurs through the hydrolysis of diethyl sulfate. The thin films demonstrate appreciable optical transmittance varying between 40 and 70% at 500 nm in dependence on the film thickness. The film structure, morphology, electrochemical behavior and electrochromic activity of fresh and aged thin films are...

Acknowledgment

The authors thank the Bulgarian Academy of Sciences and the Macedonian Academy of Sciences and Arts for the financial support and the Alexander von Humboldt Foundation for providing the electrochemical equipment....

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Effect of synthesis conditions on morphology, crystal structure and electrochemical properties of β-Na_xV₂O₅
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Different ion-based electrolytes for electrochromic devices: A review
2022, Solar Energy Materials and Solar Cells

Citation Excerpt :
...They believe that the Na^+ ($or\ Li^+$) insertion will cause the WO3 to form a cubic intercalation phase, and the inserted non-oxygen bond formation destabilizes the transition-metal framework and then gradually shrinks, distorts and finally collapses in a monoclinic phase [125]. For large radius Na^+ as electrolyte ions, ions intercalation E^+ materials with layered structure such as V2O5 showed obvious advantage in EC performance than Li^+ [126–128]. Eun Ems et al. compared the EC performance of V2O5 hybrid films in 1 M $NaClO_4$/PC and 1 M $LiClO_4$/PC, the films showed higher optical modulation and larger CE in Li^+-based conduction medium, while faster reduction responses [2,24c] were seen in Na^+-based electrolyte [129,...

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Preparation and electrochemical performance of binder-free sodium vanadium bronze thin film electrodes based on a low temperature liquid phase deposition method
2020, Materials Chemistry and Physics

Citation Excerpt :
...Besides, it retained 94% of the initial capacity after 3000 cycles at the higher rate of 5C (1250 mA g−1). Many types of synthesis methods for NaV_2O_5 have been performed to improve its electrochemical performances, including sol-gel method [18], chemical bath deposition [29,30], hydrothermal method [1,19–24,26], solvothermal reaction [25], chemical switch method [31,32] and chemical solution deposition [33]. Table 1 summarizes the literatures on the preparation of sodium vanadate in recent years, not only including the synthesis methods, but also including the crystal morphologies,...

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Development of aluminum and zirconium based xerogel for defluoridation of drinking water: Study of material properties, solution kinetics and thermodynamics
2018, Journal of Environmental Chemical Engineering

Citation Excerpt :
...$Al(OH)_3$[50]; on the other hand, shows exothermic peaks at 250 °C and 330 °C indicating a possible recrystallization of materials at higher temperature that could happened after elimination/removal of water/adsorbed molecules from core structures. Similar kind of observation was also reported by Najdoski et al. [28] while studying vanadium(V) oxide xerogel. In order to understand the material degradation kinetics which can be helpful in material fabrication technology, various kinetic parameters were evaluated using a number of kinetics models,...

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Fast electrochromic response for RF-magnetron sputtered electrospun V<inf>2</inf>O<inf>5</inf> mat
2016, European Polymer Journal

Citation Excerpt :
...Vanadium oxide and derived compounds have attracted much attention because of their interesting electrochemical performance, valuable chemical and physical properties [1,2]....

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2021, 2021 20th International Conference on Electrical Engineering, Computing Science and Automatic Control, CCE 2021

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