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A simple chemical method for deposition of electrochromic potassium manganese oxide hydrate thin films

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Abstract

A new chemical method for fast deposition of electrochromically active thin films of birnessite-type potassium manganese oxide ($K_{0.27}MnO_2{\cdot}xH_2O$) has been developed. The chemical deposition has been performed at room temperature by a reaction of aqueous solutions of potassium permanganate and manganese(II) chloride. The prepared thin films have thickness from 50 to 250 nm depending on the number of the deposition cycles. The composition and the structure of the K-birnessite films are studied by XRD, IR spectroscopy and TG/DTA analyses. Electrochemical studies using four different electrolytes such as aqueous K_2SO_4, Li_2SO_4, KNO_3, and LiClO4 in PC have been performed. The electrochromic activity has been explored by cyclic voltammetry and VIS spectrometry. The best electrochromic properties are obtained using aqueous KNO_3, where the difference in the transmittance at 400 nm between the bleached and colored state is 40% for both as-deposited and annealed films. The obtained data allow the prepared K-birnessite thin films in aqueous KNO_3 electrolyte to be proposed as a promising system for electrochromic applications.

Graphical abstract

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Highlights

► A new method for deposition of electrochromic $K_{0.27}MnO_2{\cdot}xH_2O$ thin films is developed. ► The deposition has been performed by a reaction between $KMnO_4$(aq) and $MnCl_2$(aq). ► The films exhibit electrochromism changing the color from brown to pale yellow. ► The achieved difference in the transmittance of bleached and colored state is 40%. ► The best electrochromic properties are obtained by using aqueous KNO_3 solution.

Introduction

The studies on manganese oxide thin films gain increasing importance due to their promising properties for wide range of applications. The use of manganese oxide films as ion-exchangers [1], electrode materials in capacitors [2], [3], counter electrodes [4], and supercapacitors [5], [6] is widely discussed. However, only a few studies regarding the electrochromic properties of manganese oxide thin films has been reported [7], [8], [9].

Thin films of MnO_2 have been prepared by variety of methods including electrodeposition from aqueous solution of manganese sulfate [7], [10], [11], sol–gel methods [9], [12], RF sputtering technique [13], [14], etc. The direct deposition of oxide thin films from aqueous solutions is an attractive technique because it is simple, low cost and enables to fabricate films on non-conducting, non-planar, porous, and less refractory substrates [15]. Using chemical bath deposition from solution containing $MnCl_2$ and $NaBrO_3$ at temperature 50–70 °C for 24 h. Unuma et al. [16] prepared manganese oxide films with different structure depending on the pH of the solution. Thus, γ-MnO_2 was obtained at pH of 4.8, while at pH about 7.5 the films were mixtures of Mn_3O_4, β-MnOOH, and γ-MnOOH. More recently, layered birnessite-type manganese oxide thin films for supercapacitor application were directly grown from solution containing $KMnO_4$ and NH_3 for 12 h [17].

In the present paper we describe a new chemical deposition method for the preparation of K-birnessite thin films with electrochromic properties by successive immersion of the substrates in aqueous solutions of $MnCl_2$ and $KMnO_4$. To the best of our knowledge there are no data on the electrochromic behavior of K-birnessite thin films. The method is very fast and films with thickness of 100 nm and 250 nm can be obtained for about 2–5 min. The structure, electrochemical, and optical properties of the as-deposited films are studied and compared to that of the annealed film.

Section snippets

Experimental

The commercially available fluorine doped tin oxide (FTO) glass substrates for the deposition of the films are characterized by sheet resistance of about 10–20 Ω/□ and transparency of about 80% for visible light. Before the deposition, the substrates are immersed in hexane and acetone in order to be degreased in ultrasonic bath, and then rinsed with deionized water and dried in air.…

Composition, structure, and morphology

The XRD pattern of the as-deposited thin film is shown on Fig. 1a. It exhibits a high background typical of poorly crystalline phase and only two very broad peaks are visible. The positions of these peaks agree well with the two strongest peaks characteristic of hexagonal K-birnessite with composition $K_{0.22}MnO_2{\cdot}0.54H_2O$ [JSPDS 86-666]. More probably, our sample has very similar composition. Birnessite-type structure with monoclinic or hexagonal symmetry consists of single sheets of edge-sharing…

Conclusions

A new simple method for chemical deposition of electrochromically active K-birnessite thin films is developed. The as-deposited film comprises hydrated $K_{0.22}MnO_2{\cdot}1.4H_2O$ with interlayered distance of 7.31 Å, which on annealing at 400 °C transforms into anhydrous K-birnessite (5.76 Å interlayered space). The prepared films have thickness in the range from 50 to 280 nm depending on the number of the deposition cycles. The AFM study evidences that the film surface is fully populated with particles…

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> …Hydrated K0.27MnO2. films can change color from the bleached (yellow) and colored (brown) states in aqueous KNO3 electrolyte, and the optical modulation was superior to that in LiClO4 electrolyte (Fig. 12b) [146]. In fact, not many ECMs are available for K+ due to the limitation of its large ionic radius,…

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> …Mixed oxides based on V–MV have been investigated with MV being C [559], Na [560], Ti [561,562], Mo [563,564], Ag [554], Ta [552] and W [565], and on V2O5–PEO hybrids [566]. Data have been presented also on the electrochromism in films of oxides of Co [567], Cu [568–570], Sn [571] and Zr [433], and on K0.27MnO2.nH2O [572], LixFePO4 [573], (As2W19MgO62)18− (magnesium-substituted tungsten arsenate) [574] and ZnO + ZnS/OH)8Cl2 [575]. Recent investigations on the complex oxide Bi0.9Ca0.1FeO3−0.05 are of much interest, particularly from a theoretical point of view, and indicate that vacancy-order melting can lead to intense electrochromism [576].…

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