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Hydrothermal synthesis of electrode materials Pyrochlore tungsten trioxide film

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Abstract

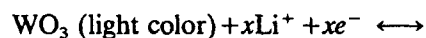
Hydrothermal synthesis methods have been successfully used to prepare new transition-metal oxides for cathodes in electrochemical devices such as lithium batteries and electrochromic windows. The tungsten oxides were the first studied, but the method has been extended to the oxides of molybdenum, vanadium and manganese. Sodium tungsten oxide films with the pyrochlore structure have been prepared on gold/alumina and indium-doped tin oxide substrates. These films reversibly and rapidly intercalate lithium and hydrogen ions.

Keywords: Tungsten oxides; Cathodes; Synthesis

1. Introduction

Although substantial progress has been made in the development of secondary lithium batteries, there is still no suitable cathode for large-scale cells such as needed for electric vehicles where active material cost is much more restrictive than in small consumer batteries such as in the Sony lithium-ion cells using cobalt or nickel oxides. All present cathode materials react with lithium by an intercalation mechanism [1,2], in which lithium ions insert themselves into the oxide host lattice. This mechanism requires fast diffusion of lithium within the lattice, which in turn dictates that the crystal structure must be fairly open or easily expanded. As such structures may not be stable at high temperatures, they must be synthesized at lower temperatures than normally possible using direct synthesis. We have embarked on a program using mild hydrothermal methods, in which the reactants are heated up to 200 °C normally in aqueous solution in sealed reaction vessels [3]. This program placed initial effort on the oxides of tungsten, because it was known that a variety of different crystalline structures could be formed. Subsequently, effort was placed on lighter elements such as molybdenum [4–6], vanadium and manganese that might be more practical for lithium-battery applications.

Hydrothermal methods can lead to fine powders or single crystals, but to our knowledge this technique has not been previously used to prepare tungsten oxide films. In this paper we discuss the formation of supported tungsten oxide films, characterized and evaluated them for possible use as cathodes in lithium batteries and electrochromic cells. Tungsten trioxide has drawn considerable attention for its electrochromism and is the most investigated electrochromic material [7–9]. The coloration process is usually described as double injection of cations (particularly Li⁺) and electrons inside the WO₃ framework as follows [10]:



Of the two steps involved in the process, charge transfer and Li⁺-ion diffusion in the structure, the latter is usually the slower. Therefore, it is desirable to find a suitable WO₃ framework structure which would facilitate the diffusion of Li⁺. WO₃ thin films have been prepared by various routes including vacuum deposition, r.f. sputtering, sol-gel method, screen printing and electrodeposition [9]. More recently, a new modification of WO₃ with pyrochlore structure, Fig. 1, has received much attention because its three-dimensional interconnected channels [3,11–13] would be expected to allow the fast mobility of cations. We have reported that the pyrochlore WO₃ could be easily synthesized

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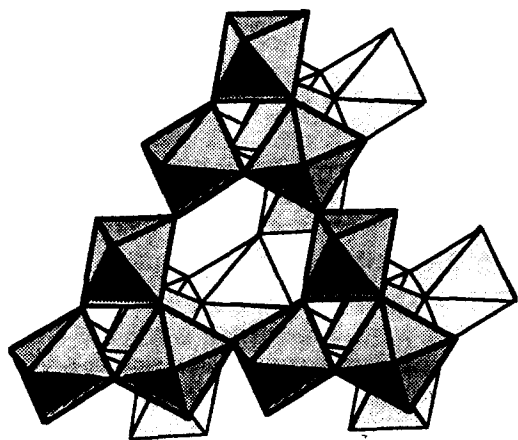


Fig. 1. Structure of pyrochlore WO_3 , showing the three-dimensional interconnected tunnels; the octahedra represent the WO_6 building blocks. The larger mobile cations such as sodium or hydronium sit at the tetrahedral site where the tunnels intersect, in the windows between the large cavities, or at sites between these two.

by mild hydrothermal methods and the facile movement of cations in the three-dimensional channels with the H_3O^+ having the highest diffusion coefficient $1.3 \times 10^8 \text{ cm}^2/\text{s}$ [14].

2. Experimental and discussion

The pyrochlore WO_3 film was prepared as described earlier [3,15]; concentrated hydrochloric acid was slowly added, with vigorous stirring, to a 1.5 M aqueous sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, Showa Chemicals Inc.) solution until the pH of the resulting mixture reached 6.0. The mixture was introduced into a pressure reactor, e.g. Parr 4748, not exceeding two-thirds capacity for safety considerations. The substrate, on to which the pyrochlore WO_3 film was to be deposited, was immersed in the mixture. The substrates utilized in this study were alumina plates coated with a layer of screen-printed gold and ITO conducting glasses (indium-doped tin oxide, Corning Inc.). The reactor was sealed and heated from room temperature to 130°C at $1^\circ\text{C}/\text{min}$, then the temperature was kept at 130°C for 24 h. The reactor was opened right after being cooled to room temperature. The product, i.e. the substrate with a deposited pyrochlore WO_3 film on the surface of it, was washed with distilled water and dried. The as-prepared film is the sodium form of the pyrochlore-type tungsten trioxide, Na-pyrochlore WO_3 , and has a chemical composition of $(\text{Na}_2\text{O})_{0.25}\text{WO}_3 \cdot z\text{H}_2\text{O}$ as determined by inductively coupled plasma-atomic emission spectroscopy and thermal gravimetric measurements with z about 0.7 and varying slightly with drying condition. The resulting film is about $50 \mu\text{m}$ in thickness, has strong mechanical property and good adhesion to the substrate. A scanning electron micrograph (Fig. 2)



Fig. 2. Scanning electron spectroscopy image of hydrothermally-grown pyrochlore WO_3 film.

shows well-crystallized polycrystals with an octahedral habit suggesting a cubic symmetry which was verified by powder X-ray diffraction measurement with a cell parameter $a = 10.270(1) \text{ \AA}$.

The lithium electrochemical cell used was a two-electrode system, pyrochlore WO_3 film on gold-coated alumina was used as cathode, lithium foil as counter and reference electrodes and 1 M LiClO_4 /propylene carbonate (PC) as electrolyte. In the case of the hydrogen cell, pyrochlore WO_3 film on ITO was the cathode, platinum foil and a saturated calomel electrode as counter and reference electrodes, respectively, and 1 M HCl was used as electrolyte. The electrochemical measurement was carried out with an EG&G VersaStat potentiostat. For the determination of the chemical diffusion coefficient of Li^+ ion, the current pulse relaxation method [16] was employed:

$$\tilde{D}_{\text{Li}} = [(i\tau(V_m)(AF\sqrt{\pi})^{-1}(dE/dx)(dE/dt^{-1/2})^{-1})^2] \quad (2)$$

where i , τ , V_m , A , and F are, respectively, the current pulse sent through the cell, the pulse duration (s), the molar volume ($36 \text{ cm}^3/\text{mol}$ for Na-pyrochlore), the electrode area (1 cm^2) and the Faraday constant; dE/dx is the local slope of coulombic titration curve and $dE/dt^{-1/2}$ is the slope of straight line obtained from the relaxation potential versus $t^{-1/2}$ after the current pulse. The current pulse applied in this experiment was 0.1 mA and the pulse duration 10 s .

After a small amount of lithium discharge into the WO_3 film ($x < 0.01$ where x is given by $\text{Li}_x\text{Na}_y\text{WO}_{3+y/2}$), the cell was subjected to electrochemical measurements. Typical cyclic voltammograms at dif-

ferent scanning rates between 1.5 and 4.0 V versus lithium for an as-synthesized pyrochlore WO_3 film are shown in Fig. 3(a), only well-resolved anodic peaks were observed as noticed for WO_3 films prepared by other methods. As the scanning rate increases, the peak height increases smoothly and eventually reached a maximum where neither peak height nor peak position was dependent on scanning rate, suggesting that the process was diffusion controlled. In association with the redox reaction, the WO_3 film exhibited reversible color changes from colorless to dark blue between 1.5 and 4.0 V. The color change was easily seen and switching from colorless to dark blue was achieved within 10 s. The reversibility was also tested by cycling between 1.5 and 4.0 V versus lithium; no deterioration of electrochromic performance was seen over several hundreds cycles. We also attempted to apply the same hydrothermal technique to grow a pyrochlore WO_3 film on ITO glass. A similar cyclic voltammogram was observed for hydrogen insertion to give $\text{H}_x\text{Na}_y\text{WO}_{3+y/2}$ (Fig. 3(b)) but the film was less homogeneous and extremely thick thus making the coloration bleaching difficult to observe.

The chemical diffusion coefficient of the Li^+ ion into the pyrochlore structure was found to be $1.1 \times 10^{-7} \text{ cm}^2/\text{s}$ at lower x ($x \approx 0.01$), which is among the highest \bar{D}_{Li} reported so far. Looking at the structure, the

interconnected three-dimensional channels in pyrochlore WO_3 (Fig. 1) should provide ample diffusion paths for Li^+ , but the exact diffusion path is not clear yet as the lithium sites have not been determined. As the films synthesized here are hydrated, water may play an important role to enhance the diffusion of Li^+ as it does for H^+ [14]. As the lithium content, x , increases, the diffusion coefficient dropped dramatically, e.g. to $1 \times 10^{-10} \text{ cm}^2/\text{s}$ at $x=0.5$. This may be related to the water content or to the number of vacant sites in the tunnels; similar observation were reported for hexagonal Li_xWO_3 and $\text{Li}_x\text{K}_{0.26}\text{WO}_3$ [17,18]. The films became highly electronically conducting on lithium insertion as expected for a tungsten bronze which exhibit metallic properties; the cyclic voltammograms showed pure ohmic behavior at $x=0.5$.

3. Summary

We have shown that homogeneous and stable tungsten trioxide films exhibiting good electrochromic properties can be prepared by direct hydrothermal approach. The chemical diffusion coefficient of the Li^+ ion was determined to be $1.1 \times 10^{-7} \text{ cm}^2/\text{s}$ which is among the highest values reported for WO_3 films. Efforts are currently underway to optimize the hydrothermal deposition and control the film thickness on both alumina/gold and ITO substrates. Similar insertion behavior has also been found for the hexagonal and monoclinic forms of molybdenum trioxide, which are expected to show interesting cathodic behavior in lithium batteries.

Acknowledgements

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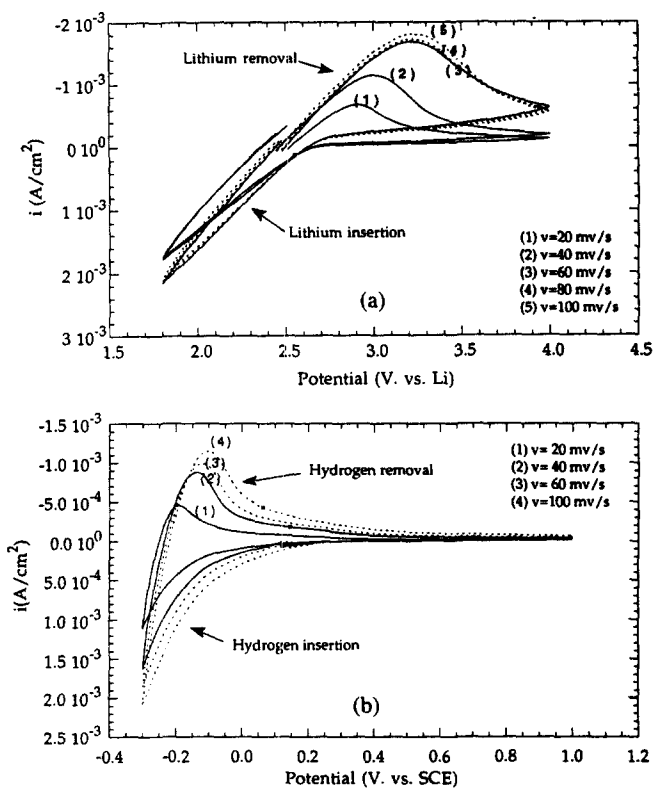


Fig. 3. (a) Cyclic voltammograms of pyrochlore WO_3 at different scanning rates in 1 M LiClO_4 /propylene carbonate. (b) Cyclic voltammograms of pyrochlore WO_3 on indium-doped tin oxide in 1 M HCl .

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