High electrochromic performance of co-sputtered vanadium–titanium oxide as a counter electrode

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ABSTRACT

This study examined the material and electrochromic properties of vanadium–titanium oxides (V–Ti oxides) as a counter electrode material in electrochromic devices. These oxides were deposited on an ITO substrate using a co-sputtering method at different levels of RF power. Electrochemical experiments of these oxides were carried out using half-cell and semi full-cell tests which are good methods for measuring the potential applied to each electrode. The change in electrochromic properties after 1000 cycles of a semi full-cell test was examined. Reversibility and durability of an electrochromic device were improved by increasing the titanium content in V–Ti oxides.

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1. Introduction

Materials with optical properties that can be changed by external stimulation (light, change of temperature and electric potential) are called chromogenic. The first report of an electrochromic material, tungsten oxide, was published approximately 40 years ago by Deb [1]. Initially, the optical absorption of a visible ray can be changed broadly by the absorption and emission of an electrical charge. Electrochromism has attracted considerable attention in research. In the mid-1980s, there was some interest in placing large windows on the ceiling of buildings. The interest in electrochromism was increased significantly by the concept of a 'smart window', which was invented to reduce energy consumption in buildings [2].

For electrochromic materials, there are many species, such as organic, inorganic and metal organic complexes. Among them, the electrochromic materials used in electrochromic windows are generally inorganic materials owing to the thermal stability they possess. In addition, inorganic electrochromic materials can generally be divided into two parts: cathodic coloring materials and anodic coloring materials. Cathodic coloring materials are oxides of W, Nb, Mo, Ti, Ta, etc. and anodic coloring materials are oxides of Cr, Mn, Fe, Co, Rh, Ir and Ni. Among them, tungsten trioxide (WO_3) is the material most studied. Tungsten trioxide has a similar crystal structure to perovskite [3]. The electrochromic

properties (color change, response time and reversibility of lithium intercalation) of crystal tungsten trioxide are poor. However, the electrochromic properties of amorphous tungsten trioxide are superior to any other metal oxide examined [4].

Vanadium oxide (V_2O_5) has been actively studied for use in secondary batteries [5] due to a high charge capacity. Currently, vanadium oxide is used primarily as an anodic material for electrochromic devices. However, the demerits of pure vanadium oxide (durability and transparency) make it difficult for use as a counter electrode material in an EC device. Therefore, many research groups have mixed vanadium oxide with other materials, such as titanium oxide, cerium oxide, zirconium oxide, iron oxide and nickel oxide [6–13]. Among the demerits of vanadium oxide, cycling durability is the main problem preventing commercialization. Generally, the materials used to enhance the cycling durability of a material are titanium oxide and cerium oxide [14,15]. Cerium oxide is used as an additive material for the counter electrodes of EC devices due to its transparency. Its charge capacity, however, is very low. Therefore, it is difficult to maintain a sufficient charge when the charge capacity of the working electrode is high. Titanium oxide is used as an additive material to enhance electrical conductivity and prevent crystallization of a material during cycling. Therefore, it can be used to improve cycling durability. In this study, V–Ti oxides were deposited by RF magnetron co-sputtering. The composition of vanadium and titanium was varied to control the power ratio of the two targets. The electrochemical and optical properties of these samples were measured using a half-cell test, and their cycling durability was measured using a semi full-cell test. In the case of the semi full-

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cell test, it is easy to determine the level of electrode degradation. Moreover, the potential applied to each electrode could be measured using two electrode experiments.

2. Experiment

The V–Ti oxides and tungsten oxide were deposited by RF magnetron sputtering (Korea Vacuum Tech.) onto a glass pre-coated with indium–tin oxide (ITO) with a resistance of $10\,\Omega/m$. The base pressure of the deposition chamber was 5×10^{-6} Torr. Pre-sputtering prior to deposition was carried out for more than 30 min under the same deposition conditions to clean the targets and ensure steady state deposition. The Ar pressure was maintained at 10 mTorr during pre-sputtering and sputtering. Substrate rotation (11 rpm) assured film uniformity, and the sputtering angle to the substrate was $52°$.

Vanadium oxide thin film was prepared using a V_2O_5 target. Sputtering deposition was carried out at 300 W RF power for 2 h. The V–Ti oxide thin films were prepared by co-sputtering V_2O_5 and TiO_2 targets. Co-sputtering deposition was carried out for 2 h with 300 W RF power to the V_2O_5 target, and with 80, 130, 200 and 300 W RF power to the TiO_2 target. Tungsten oxide thin films used as the counter electrodes of the full-cell were also prepared by RF magnetron sputtering using a WO_3 target with 150 W RF power for 52 min. The deposition conditions and film thickness of the tungsten oxide films (400 nm) were optimized in previous work [16].

The compositions of the deposited films were measured by energy dispersive X-ray spectroscopy (EDS, JSM 6700F) and electron probe X-ray micro analyzer (EPMA, JXA-8900R). Field emission scanning electron microscopy (FE-SEM, JSM 6700F) was used to measure film thickness and surface structure. The structures of the films were examined by X-ray diffraction (XRD, D-MAX2500-PC).

The electrochemical and electrochromic properties and optical properties of the deposited films were measured using a potentiostat/galvanostat (AUTOLAB PGSTAT30) and He/Ne laser ($\lambda = 632.8$ nm), respectively. The electrochemical techniques used in this study were the cyclic voltammetry (CV) and the chronocoulometry (CC), which measured the Li^+ intercalation/deintercalation potential and charge capacity of the films, respectively. CC was also used to test the operation for 1000 cycles. In these electrochemical experiments, 1 M $LiClO_4$ in propylene carbonate was used as the electrolyte. In the case of the half-cell test, the working electrode was connected to V–Ti oxide. The reference and counter electrodes were connected to Ag/AgCl (sat. KCl) and Pt wire, respectively. In the semi full-cell test (the two electrode experiments), the working and counter electrodes were tungsten oxide and V–Ti oxide thin films, respectively. In this case, with the Ag/AgCl (sat. KCl) not connected to the potentiostat, it was immersed in the electrolyte, and a digital voltmeter was used to measure the voltage between the Ag/AgCl and the working electrode (tungsten oxide). The *in-situ* optical properties were determined during the electrochemical experiment using a He–Ne laser.

3. Results and discussion

Table 1 shows the atomic ratios as measured by EDS and EPMA and film thicknesses as measured by FE-SEM of the V–Ti oxides. The titanium content in the V–Ti oxide films increased with the increasing sputtering power to the titanium oxide target but the tendency of the increase was not linear. The Ti/V ratio of the sample with the same sputtering power applied to both targets

Table 1

Abbreviations of the V–Ti oxides, compositions of the V–Ti oxides by EDS and film thicknesses of the V–Ti oxides by FE-SEM.

Abbreviations	RF power of V_2O_5 (W)	RF power of TiO_2 (W)	Ti:V atomic ratio	Film thickness (nm)
V_2O_5	300	0	0:100	270
VTi01	300	50	1:99	163
VTi07	300	80	7:93	177
VTi17	300	130	17:83	158
VTi33	300	200	33:67	186
VTi44	300	300	44:56	202

(300 W) was 0.8. Therefore, the co-sputtering yields of vanadium oxide and titanium oxide can be considered similar. Abbreviations of the samples are shown in Table 1.

Fig. 1 shows the surface FE-SEM images of VTi01, VTi17 and VTi44. The figure also shows the surface morphology of the V–Ti oxides and the boundaries of the oxide lumps. These surface morphologies may allow the lithium ions to intercalate into the oxide film. However, the boundaries of the VTi44 oxide lumps appeared faint, and the surface morphology of the VTi44 was denser than that of the VTi01. The FE-SEM images suggest that the intercalating rate of lithium ions into the VTi01 film would be faster than it was into the VTi44 film.

Fig. 2 shows the XRD patterns of the V–Ti oxides. Every XRD pattern showed ITO peaks because the film thickness was at most 270 nm and the substrate was ITO glass. With the exception of ITO, none of the patterns of the V_2O_5 and V–Ti oxides showed crystal peaks. Therefore, these results showed that V_2O_5 and V–Ti oxides have an amorphous structure.

Fig. 3(a) shows the results of cyclic voltammetry. The current density in the cyclic voltammograms of the samples containing a large amount of vanadium was high due to the charge capacity. In addition, the anodic current peaks were quite broad. These broad peaks were shown in typical cyclic voltammograms of V_2O_5 when the scan rate was relatively fast (20 mV/s) [17]. Fig. 3(b) shows the electrochromic properties measured using the half-cell test (charge capacity and optical transmittance modulation). In the present study, the charge capacity was measured by chronocoulometry. Therefore, the charge capacity expressed in this paper is not the precise meaning of 'charge capacity' but, rather, it is the 'degree of ease' of Li^+ ion intercalation/deintercalation. The charge capacities of the V–Ti oxides were maintained at more than 37.6 mC/cm^2 until the titanium content was 33 at%, and an abrupt decrease in charge capacity was observed at a titanium content of 44 at%. The aspect of ΔT at different titanium contents was similar to that observed for the charge capacity. The only difference was an abrupt decrease in ΔT at low titanium content. Originally, both vanadium oxide and titanium oxide showed cathodic coloration. These transmittance modulations are undesirable when used as a counter electrode for tungsten oxide in an EC device. Therefore, in V–Ti oxide, even a small amount of titanium is desirable for use as a counter electrode.

An electrochromic full-cell test was carried out using V–Ti oxide and a semi full-cell test was carried out using tungsten oxide. After conducting the half-cell test of V–Ti oxide, the tungsten oxide was fully reduced, containing lithium ions, and the V–Ti oxide was fully oxidized. The semi full-cell was constructed as shown in Fig. 4. The tungsten and V–Ti oxides were connected to the working and counter electrodes, respectively. The initial semi full-cell test was operated for 5 cycles by applying +1.5 V for 30 s and −1.5 V for 30 s. During this test, the optical transmittance