All-solid-state electrochromic device composed of WO3 and Ni(OH)2 with a Ta2O5 protective layer
Kwang-Soon Ahn, Yoon-Chae Nah, Yung-Eun Sung, Ki-Yun Cho, Seung-Shik Shin et al.

Citation: Appl. Phys. Lett. 81, 3930 (2002); doi: 10.1063/1.1522478
View online: http://dx.doi.org/10.1063/1.1522478
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v81/i21
Published by the American Institute of Physics.

Additional information on Appl. Phys. Lett.
Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT

Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities fast

www.goodfellowusa.com
All-solid-state electrochromic device composed of WO$_3$ and Ni(OH)$_2$ with a Ta$_2$O$_5$ protective layer

Kwang-Soon Ahn, Yoon-Chae Nah, and Yung-Eun Sung

Department of Materials Science and Engineering, Kwangju Institute of Science and Technology (K-JIST), Kwangju 500-712, S. Korea

Ki-Yun Cho, Seung-Shik Shin, and Jung-Ki Park

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejon 305-701, S. Korea

(Received 24 July 2002; accepted 26 September 2002)

An all-solid-state electrochromic device composed of WO$_3$ and Ni(OH)$_2$ with a Ta$_2$O$_5$ protective layer was prepared by rf magnetron sputtering and lamination with a proton-conducting solid polymer electrolyte. This device had good durability, high transmittance modulation (18%–74%) and coloration efficiency (about 84 cm$^2$ C$^{-1}$), and good response times (8.5 and 18 s, respectively, during the bleaching and coloring processes). This indicates that Ta$_2$O$_5$ layers are electrochemically stable and can be used as protective layer for Ni(OH)$_2$ as well as WO$_3$. © 2002 American Institute of Physics. [DOI: 10.1063/1.1522478]

Electrochromism (EC) is defined as a phenomenon in which a change in color (light transmittance) takes place in the presence of an applied voltage.\textsuperscript{1–3} Because of their low power consumption (<2 V), high coloration efficiency, and memory effects under open circuit conditions, EC devices have many potential applications in smart windows, mirrors, displays, and optical switching devices.\textsuperscript{1–3} An EC device generally consists of a transparent electrically conducting layer, electrochromic cathodic and anodic coloring materials, and an ion conducting electrolyte. Such devices are currently prepared using proton-conducting solid polymer electrolytes (H$^+$–SPE) for practical use, because of the advantages of this process, which involves seal development during manufacture and the inhibition of bubble formation.\textsuperscript{1,4} WO$_3$ and Ni hydroxide are currently in widespread use as, respectively, cathodic and anodic coloring materials.\textsuperscript{1,2,5–9} However, EC devices incorporating WO$_3$ and Ni(OH)$_2$ may have problems related to their limited durability due to chemical incompatibility between the electrochromic layers and the adjoining electrolyte.\textsuperscript{10,11} WO$_3$ is stable in a moderately acidic electrolyte but rapidly dissolves in a basic electrolyte. On the other hand, the Ni(OH)$_2$ is stable in a basic electrolyte but unstable in an acidic electrolyte. Recently, a solution to this problem was attempted by depositing a compact WO$_3$ protective layer on top of the Ni hydroxide.\textsuperscript{10,12} However, the WO$_3$ also has a tendency to slowly dissolve in an acidic electrolyte because hydrated WO$_3$, the soluble form, is formed during the bleaching/coloring processes in the acidic electrolyte,\textsuperscript{1,13} which may lead to the degradation in the performance of an EC device.

Ta$_2$O$_5$ was used to protect the WO$_3$ in an EC system comprised of indium tin oxide (ITO)/WO$_3$/H$^+$–SPE/Ir oxide/ITO,\textsuperscript{1,2} in which Ir oxide, the electrochromic anodic coloring material, is stable in an acidic electrolyte but has a much lower coloration efficiency (CE) of about 17 cm$^2$ C$^{-1}$ than that (about 37 cm$^2$ C$^{-1}$) of Ni hydroxide,\textsuperscript{1} thus limiting the practical use of the Ir oxide in EC devices. Ta$_2$O$_5$ may represent another possible protective layer on top of the Ni(OH)$_2$.

In this letter, an all-solid-state, proton-based EC device with a Ta$_2$O$_5$ protective layer on top of the Ni(OH)$_2$ layer was fabricated and its performance compared with a similar EC device but without a Ta$_2$O$_5$ protective layer on top of the Ni(OH)$_2$. The EC device composed of spin-on-glass (SOG) (a kind of thermally decomposed SiO$_2$)-coated glass/ITO/Ni(OH)$_2$/Ta$_2$O$_5$/H$^+$–SPE/Ta$_2$O$_5$/WO$_3$/ITO/SOG-coated glass provided good durability, a high CE, and an acceptable response speed, due to the protective property of the Ta$_2$O$_5$ between the Ni(OH)$_2$ and the acidic polymer electrolyte.

Two types of all-solid-state EC devices comprised of SOG-coated glass/ITO/Ni(OH)$_2$/H$^+$–SPE/Ta$_2$O$_5$/WO$_3$/ITO/SOG-coated glass and SOG-coated glass/ITO/Ni(OH)$_2$/Ta$_2$O$_5$/H$^+$–SPE/Ta$_2$O$_5$/WO$_3$/ITO/SOG-coated glass were fabricated, shown as (a) EC1 and (b) EC2 in Fig. 1. First, NiO and WO$_3$ films were deposited on the substrates of ITO coated SOG-coated glass. NiO and W metal were used as target materials. The working pressures were 5×10$^{-3}$ Torr and 2×10$^{-2}$ Torr, respectively, for the NiO and WO$_3$ sputtering and the sputtering was performed under Ar:O$_2$ ratio of 1:1 and only O$_2$, respectively. The NiO and WO$_3$ films were sputter-deposited at rf powers of 60 and 100 W, respectively, for 90 min at RT, the detailed deposition procedures for which have been reported elsewhere.\textsuperscript{8,9,14} Ta$_2$O$_5$ protective films were then deposited on the NiO/ITO/SOG-coated glass and WO$_3$/ITO/SOG-coated glass using a rf magnetron sputtering system. Ta$_2$O$_5$ was used as the target material. The base pressure was below 5×10$^{-6}$ Torr, the working pressure was 5×10$^{-3}$ Torr, and the sputtering was performed under only O$_2$ at 40 sccm. Prior to sputtering, a presputtering process was performed for 20 min in order to remove contaminants from the target. Sputtering was then conducted at a rf power of 60 W for 10 min at RT.
Ni(OH)\(_2\)/ITO/SOG-coated glass and Ta\(_2\)O\(_5\)/Ni(OH)\(_2\)/ITO/SOG-coated glass was prepared by the potential cycling of the sputter-deposited NiO/ITO/SOG-coated glass and Ta\(_2\)O\(_5\)/NiO/ITO/SOG-coated glass, respectively, in a 1 M NaOH electrolyte.\(^8,9,15\) The thicknesses of the sputter-deposited Ta\(_2\)O\(_5\), NiO, and WO\(_3\) layers were about 60, 300, and 200 nm, respectively, as determined by cross-sectional scanning electron microscopy (SEM). The crystallographic microstructures of all the deposited films were amorphous, as evidenced by x-ray diffraction data. Finally, all-solid-state EC1 and EC2 devices in Fig. 1 were fabricated by laminating the sulfonated styrene–ethylene–butylene–styrene triblock copolymer used as the H\(^+\)–SPE, which was described elsewhere.\(^16\)

Both EC1 and EC2 devices were tested after storage in atmosphere for 2 days to estimate their durability. EC properties such as the CE and response time were evaluated by switching a pulse potential wave between –1.7 and 1 V (versus anodic coloring material) with a duration time of 30 s, referred to as switched pulse potential cycling. The transmittance (633 nm) was simultaneously measured \textit{in situ} during potential cycling, as described elsewhere.\(^8,14,15\)

The EC properties of Ta\(_2\)O\(_5\)/Ni(OH)\(_2\)/ITO/SOG-coated glass and Ta\(_2\)O\(_5\)/WO\(_3\)/ITO/SOG-coated glass were first investigated by electrochemical cell tests, for comparison to those of an all-solid-state EC device. The Ta\(_2\)O\(_5\)/Ni(OH)\(_2\)/ITO/SOG-coated glass and Ta\(_2\)O\(_5\)/WO\(_3\)/ITO/SOG-coated glass were used as working electrodes in typical three-electrode electrochemical cell, where Pt wire and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively.\(^8,9,14,15\) Figure 2 shows \textit{in situ} transmittance curves obtained during the switched pulse potential cycling tests for the electrochemical cells of (a) Ta\(_2\)O\(_5\)/Ni(OH)\(_2\)/ITO/SOG-coated glass and (b) Ta\(_2\)O\(_5\)/WO\(_3\)/ITO/SOG-coated glass electrochemical cells. The electrochemical cells of Ta\(_2\)O\(_5\)/Ni(OH)\(_2\)/ITO/SOG-coated glass and Ta\(_2\)O\(_5\)/WO\(_3\)/ITO/SOG-coated glass had CE values of about 37 and 45 cm\(^2\) C\(^{-1}\), respectively, in which CE is defined as \(\log(\frac{T_{\text{bleached}}}{T_{\text{colored}}})/Q\) where \(T_{\text{bleached}}\) and \(T_{\text{colored}}\) are the transmittances of the bleached and colored states, and \(Q\) is charge per unit area used during the coloring process. The response times during the bleaching/coloring processes were also quantitatively calculated from the normalized first transmittance curves of the switched pulse potential cycling.\(^8,9,14,15\) The EC response time was calculated on the level of a 90% transmittance change. The response times during the bleaching and coloring processes were about 5 and 17 s, respectively, for the Ta\(_2\)O\(_5\)/Ni(OH)\(_2\)/ITO/SOG-coated glass electrochemical cell and about 6 and 18 s, respectively, for the Ta\(_2\)O\(_5\)/WO\(_3\)/ITO/SOG-coated glass electrochemical cell. The coloring response time was, on the whole, slower than the bleaching response time, because the conductivities of the bleached-state forms, Ni(OH)\(_2\) and WO\(_3\), are lower than those of the colored-state forms, NiOOH and HWO\(_3\).\(^8,14\)

Figure 3 shows \textit{in situ} transmittance curves obtained during the switched pulse potential cycling performed after storage for 2 days for the all-solid-state EC devices. For the
modulation the other hand, the EC2 device showed good transmittance detailed studies of this are currently underway.

The bleaching response time of the EC2 device is longer than the bleaching and coloring processes of the EC2 device were about 8.5 and 18 s, respectively. The response times during the bleaching and coloring processes of the EC2 device were about 8.5 and 18 s, respectively. The bleaching response time of the EC2 device is longer than those of the electrochemical cells shown in Fig. 2, indicating the existence of other, as yet unknown, rate-limiting factors. The coloring response time of the EC2 device is similar to those of the electrochemical cells shown in Fig. 2, indicating that Ta2O5 protective layer in itself was not the rate-limiting factor for the EC2 device. Instead, the relatively lower ion conductivity of the H+ – SPE compared to that of the aqueous electrolyte or poor interfacial property between the Ta2O5 and the H+ – SPE may act as rate-limiting factors. Detailed studies of this are currently underway.

In summary, an all-solid-state EC device composed of WO3 and Ni(OH)2 with Ta2O5 protective layer, SOG-coated glass/ITO/Ni(OH)2/Ta2O5/H+ – SPE/Ta2O5/WO3/ITO/SOG-coated glass, was prepared by rf magnetron sputtering and lamination, the EC properties of which were estimated from a comparison with the electrochemical cells of Ta2O5/Ni(OH)2/ITO/SOG-coated glass and Ta2O5/WO3/ITO/SOG-coated glass, respectively, and an all-solid-state EC device without the Ta2O5 protective layer on top of Ni(OH)2. The EC device without the Ta2O5 protective layer on top of Ni(OH)2 scarcely showed any transmittance modulation, due to dissolution of the Ni(OH)2. On the other hand, the EC device with the Ta2O5 protective layer on top of Ni(OH)2 had a good durability, high transmittance modulation (18%–74%) and a CE value (about 84 cm2 C–1), and a good response speed of 8.5 and 18 s, respectively, during the bleaching and coloring processes. Therefore, we conclude that the Ta2O5 layer is electrochemically stable and can be used as a viable protective layer on top of the Ni(OH)2 as well as WO3. Although more detailed studies of the Ta2O5 protective layer are required, we expect that it will be useful as a durable smart EC window with a high CE and a good response time.

This work was supported by Grant No. 2000-30700-003-1 from the Basic Research Program of the Korea Science and Engineering Foundation and the Brain Korea 21 Project.

1 C. G. Granqvist, Handbook of Inorganic Electrochromic Materials (Elsevier, Amsterdam, 1995)