Laminated all-solid state NiO/WO_3 complementary electrochromic device*

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Abstract Based on the previous studies on the rf reactive sputtered nickel oxide film with nanostructure and its electrochromism, i.e. electrochromic effect of the films is attributed to the reversible change of the non-stoichiometry in the nanocrystalline grain boundaries and interfaces due to the injection and ejection of Li^+ ions, a prototype of all-solid-state NiO/WO_3 complementary electrochromic device using Li_xTaO_y thin film as inorganic electrolyte was designed and prepared. The results indicate that the solar reflectance of the device could be modulated from 0.15 in colored state to 0.60 in bleached state with excellent cyclic reversibility, durability and high response speed (less than 0.3 s from colored state to bleached state).

Keywords: Smart Windows, all-solid-state electrochromic device, nickel oxide thin films, tungsten oxide thin films.

In the recent decade, a considerable interest has been focused on the electrochromic materials and devices for potential applications in displays and energy efficient window systems for the buildings and automobiles, known as Smart Windows, to control the amount of solar radiation into the glazing[1,2]. In our previous papers[3,4], we reported a kind of rf reactive sputtered nickel oxide thin films showing excellent electrochromic properties and proposed a new electrochromic mechanism to explain its colour and bleach process. According to this mechanism, the electrochromic reaction of the films can be attributed to the reversible change of non-stoichiometric composition caused by the Li^+ ion intercalation/deintercalation in the nickel oxide films[5] and it can be written as follows:

The initial bleach reaction:

$$Ni_{1-x}O \text{ (as-deposited)} + yM^+ + ye^- \rightarrow M_yNi_{1-x}O \text{ (bleached)}.$$

The reversible electrochromic reaction:

$$M_yNi_{1-x}O \text{ (bleached)} \leftrightarrow M_{y-z}Ni_{1-x}O \text{ (colored)} + zM^+ + ze^-.$$

Here the as-deposited nickel oxide with high optical absorption was found to be rich in oxygen and M^+ represents the alkali metal ions (H^+, Li^+, Na^+, K^+).

Obviously, this reaction differs from the commonly accepted mechanism proposed in the study of electrochemical process deposited nickel oxide thin films which is represented as[6,7]:

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$$Ni(OH)_2(\text{bleached}) \leftrightarrow NiOOH\ (\text{colored}) + H^+ + e^-.$$

Further studies pointed out that the sputtered nickel oxide films with good electrochromic performance were a kind of nanostructured films with highly disordered grain-boundaries. Their grains with NaCl-type structure range from 5 to 10 nm in size[8,9]. Relating the nanostructured features of films with their electrochromic reaction, it is believed that the process of injection/extraction of alkali metal ions is one of ion diffusion along the highly disordered grain-boundaries in the nanostructured films. That causes nickel vacancies to be compensated/recovered, and the reversible non-stoichiometric reaction, which leads the films to change optical state between the transparent and the high absorbed, takes place.

Based on the cardinal principles mentioned above, an all-solid state complementary electrochromic device was designed and fabricated with a configuration: |glass|ITO|NiO|Li_xTaO_y|WO_3| metal electrode|, where the Li_xTaO_y is used as inorganic electrolyte and WO_3 as ion storage. In this paper, the preparation and the electrochromic performances of the device with an active area 5 cm × 6 cm are introduced.

1 Preparation of the all-solid state electrochromic device

The all-solid state electrochromic device composed of 4-layer thin films was prepared using a PLASSYS MP450 multi-cathode magnetron sputtering coater. First, the nickel oxide thin film was deposited onto the ITO-coated glass with sheet resistance 10 Ω/□. The as-deposited film was initially bleached under a voltage −1.5V in 1 mol/L $LiClO_4$ propylene carbonate solution. Then, the films of Li_xTaO_y, WO_3 and Al were deposited onto the bleached nickel oxide thin film successively. The deposition parameters of the nickel oxide and tungsten oxide thin films by dc reactive magnetron sputtering process have been detailed in our previous papers[3,10]. The Li_xTaO_y thin film is composed of nano-sized amorphous particles with an average size 10 nm, and its preparation and performance were described in another paper[11]. The thickness of the individual films was determined using Talystep instrument. The result is listed in table 1.

Table 1 The thickness of individual films for the device

Film	NiO	Li_xTaO_y	WO_3	Al
Thickness/nm	250	170	300	300

2 Character of all-solid state electrochromic device

2.1 Optical properties

Using Al thin film as a reflective surface, which also acts as electrode, the spectral reflectance of the device in the bleached and colored states was measured by a Varian 2300 spectrophotometer as shown in fig. 1 after 3 000 cycles by operating the device between −1.5 V and +1.5 V. The result shows that this device exhibits an excellent dynamic range and reversibility with the solar reflectance 0.60 in bleached state and 0.15 in colored state.

2.2 Cyclic voltammetry

The cyclic voltammogram of the device was investigated using an electrochemical process

measurement system made up of EG&G PAR 173 and 175. The cyclic voltammetry diagram of the device cycled in the voltage range, -1.5 V $\leftrightarrow$ $+1.5$ V, at a sweep rate 100 mV/s is shown in fig. 2. The cathode current refers to the coloring process of the nickel oxide and tungsten oxide films, in which Li^+ ions are ejected from nickel oxide film, via Li_xTaO_y electrolyte film, and injected into tungsten oxide film. The anode current refers to the bleaching process in which Li^+ ions are transported in a reverse direction.

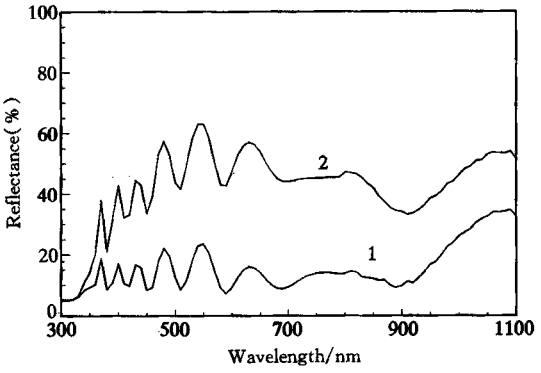

Fig. 1. The spectral reflectance of the device in bleached and colored states. 1, Colored; 2, bleached.

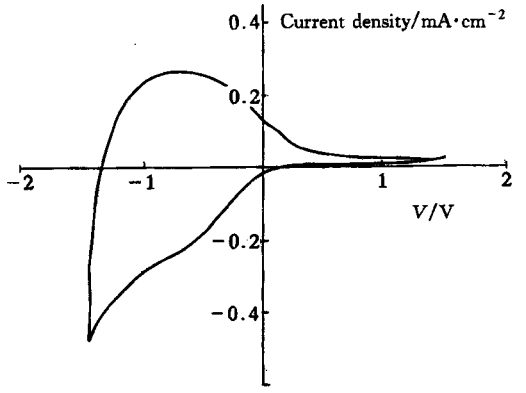

Fig. 2. The cyclic voltammogram of the device between -1.5 V and $+1.5$ V at the sweep rate 100 mV/s.

2.3 Responsibility

There are two kinds of response time for electrochromic device, namely optical and electrical responses. They can be estimated from reflectance vs. time and current vs. time respectively. In principle, both of them are representative of the same reaction process since the change in optical properties of the device is due to the ion intercalation/deintercalation according to the electrochromism. So they should have the same value. It is concluded that the response time for the tested device was less than 0.3 s both in the bleaching and coloring processes (figure 3).

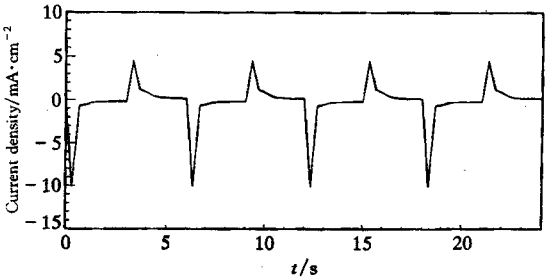

Fig. 3. The current intensity vs. cyclic time curve of the device by applying a square wave voltage between -1.5 V and $+0.5$ V with a period of 6 s.

2.4 Impedance analysis

Figure 4 shows the impedance spectroscopy data of the all-solid state WO_3/NiO device in the bleached and colored states performed by an HP 4192LP impedance analyzer. For each state, the bias voltages $+1.5$ V and -1.5 V were applied respectively. The amplitude of ac signal voltage was 10 mV and its frequency ranged from 10 Hz to 10 MHz. A parallel RC model was used for the data analysis, and its equivalent circuit is schematically plotted in fig. 5. Here R_o is the ohmic resistance due mainly to the WO_3 and NiO thin films, R_b is the bulk resistance of the Li_xTaO_y

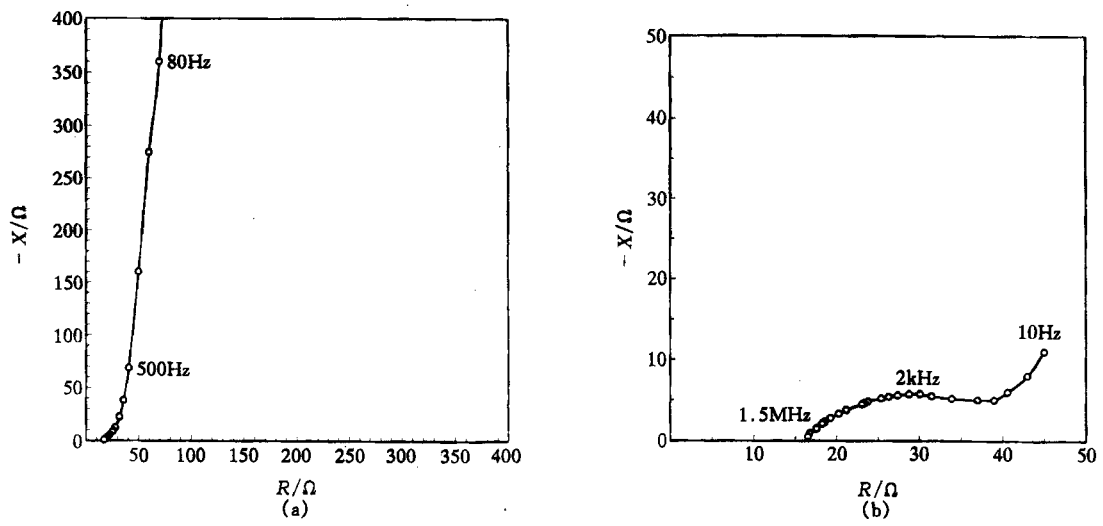

Fig. 4. The impedance diagram of the device in the bleaching (a) and coloring (b) processes with the bias voltages + 1.5 V and − 1.5 V respectively.

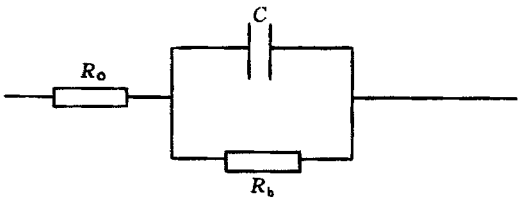

Fig. 5. The equivalent circuit of the device for impedance analysis.

electrolyte layer and C is its capacitance. The different behavior of impedance diagrams in the bleached and colored states is due to the change in conductance of the nickel oxide and tungsten oxide films in their bleached and colored states. The impedance spectroscopy data can be divided into three parts in terms of a Cole-Cole plot. In the frequency range below 500 Hz, the straight line of the plot with the constant phase angle can be related to an ion diffusion process during the electrochromic reaction. In the range from 1kHz to 1 MHz, the semicircular relationship between impedance and frequency shows a typical interface polarization process. Above 1.5 MHz, the data show that the impedance of the device is dominated by the ohmic character of the nickel oxide and tungsten oxide films, R_o. R_b for Li^+ ions migration in the Li_xTaO_y electrolyte film was about 19 Ω both in coloring and bleaching processes, and its calculated ionic conductivity was 3.3×10^{-7} S·cm^{-1}.

3 Summary

Based on the authors' new coloration mechanism of sputtered nickel oxide films, which is supposed to be a process of cationic transport, a prototype of completely all-solid state NiO/WO_3 complementary electrochromic device was successfully designed and constructed. The device using a Li_xTaO_y thin film as inorganic ion conductor exhibits the excellent dynamic range in vis-nir with solar reflectance 0.15 in colored state and 0.60 in bleached state. The experimental results of its electrochemical performances indicated that the device has high cyclic reversibility, durability and a response time less than 0.3 s. This success of the all-solid state device introduced in this paper gives an eloquent proof to coloration mechanism in sputtered nickel oxide films proposed by the authors and may help to blaze a practical trail for the future of Smart Windows.

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