The Mechanism of Trapped Ions Eroding the Electrochromic Performances of WO$_3$ Thin Films

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The electrochromic WO$_3$ devices normally suffer from the degradation of long-term performances since the accumulation of trapped ions in the host structure. In this study, we notice that the degradation of WO$_3$ film consists of the decrease of bleaching state and the decay of coloration state, and the latter is the main factor of affecting the cyclic stability of the WO$_3$ film. Here, it is discovered that the degradation of coloration state is due to the decrease of the charge density of inserted ions in the film during cycling process. By employing the open circuit potential (OCP) measurement, we find that the accumulation of trapped ions in WO$_3$ film will cause the decay of OCP between the work electrode of WO$_3$ film and counter electrode, which is the main reason of the decrease of inserted ions. This is because that the decay of OCP will weaken the electric field force used to drive ions into the film and shorten the duration time of ion insertion process. Consequently, the decline of charge density of the inserted ions will cause the decay of coloration state, which is the real mechanism of trapped ions eroding the cyclic life of the WO$_3$ film.

1. INTRODUCTION

The electrode materials based on reversible redox reaction by the insertion and extraction of small ions have been exploited in the applications for energy storage and saving such as lithium ion batteries, supercapacitors and electrochromic devices, etc.[1-3] Ion insertion process requires a number of interconnected steps involving substantial changes in the structure and electronic properties of the host materials.[4] The better understandings of the ion transport kinetics and structure stability of ion insertion materials are very important in the development of the device performances, and the design of devices. As a well-known inorganic intercalation material, WO$_3$ can display colorless and blue color by alternately applying positive and negative electrical voltages[5]. The electrochromic properties of

WO_3 are interesting when it is applied in energy-saving smart windows, antiglare mirrors, high contrast displays, and active camouflage.[6] In Li^+ ion electrolyte, the color change of electrochromic WO_3 material is believed to be directly related to the double injection/extraction of electrons and ions, and the mechanism is frequently described by a simple oxidation–reduction reaction:[7]

$$WO_3 + x(Li^+ + e^-) \leftrightarrow Li_xWO_3 \qquad (1)$$
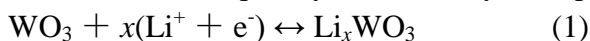
where x is the mole fraction of Li^+ inserted into WO_3 host, and e^- denotes electrons. When a negative bias potential is applied on the WO_3 film electrode, the insertion of Li^+ ions into the electrode will cause the dark blue color response. Then by employing a positive bias potential on the electrode, the color can change from dark blue to transparent state due to the extraction of Li^+ ions from the film. Large optical modulation and long-term durability are key prerequisites for practical implementation of electrochromic devices. However, WO_3 films usually suffer the degradation of optical modulation when inserted Li^+ ions are bound and cannot be completely extracted from the host structure.[8, 9] Over many cycles, these bound ions will accumulate in the film and erode the electrochromic performances. There are two different types of trap sites in WO_3 host structure which includes intermediate trap site and deep trap site[10]. When the inserted Li^+ ions diffuse into the intermediate trap sites, the ions can be completely extracted out under the action of an electric field. In the deep trap sites, the inserted ions will be trapped for long time and become immobile, which will result in the accumulation of inserted ions in the film[1, 10]. Nonetheless, real mechanism of the trapped ions corroding the optical modulation ability of electrochromic films at the subsequent electrochemical reactions is still unknown. In addition, we have noticed that the degradation is usually accompanied with the decrease of the charge density of inserted ions in film [11, 12]. However, to the best of our knowledge, there is almost no report to explain this phenomenon. In this study, by employing the open-circuit-potential (OCP) measurement, we have found out that the forming of this phenomenon is the main reason of eroding the cyclic stability of electrochromic WO_3 films.

Usually, the open-circuit-potential (OCP) measurement is frequently used to investigate various electrochemical processes, such as photoelectronic effects in semiconducting materials, secondary batteries and corrosion of metals [13]. In addition, OCP measurement has extraordinary advantage for studying the adsorbing process of neutral species and ions on electrode[14]. However, for all we know, there are few papers to explore the OCP of materials in electrochromic field. In this paper, we use the CV method to study the stability of WO_3 films under different scan rates, and the quantity of ions and OCP evolution upon cycle can be obtained by CV curves. Meanwhile, in-situ optical transmittances are recorded to observe the change of electrochromic performance of WO_3 film during OCP evolving process. By employing the relation between the quantity of charges, OCP and the electrochromic performance, this study give a definite mechanism and a new understanding for the degradation of WO_3 films.

2. EXPERIMENTAL SECTION

2.1 Preparation of samples

The amorphous WO_3 thin films were deposited on the glasses pre-coated by 120-nm-thick ITO, and the plate resistance of ITO glasses is about 17 Ω/Sq. Prior to the deposition, the substrates were

cleaned ultrasonically in industrial alcohol, deionized and then dried in air. The WO_3 films were deposited by direct-current magnetron sputtering system with the background pressure of 2.0×10^{-3} Pa and without heating equipment during deposition. The diameter of metallic W target is about 100 mm. The distance between target and rotating substrate holder is 7 cm with an incident angle of 41°. During deposition, the O_2/Ar gas-flow ratio was set at a constant value of 9 sccm/27 sccm. The total pressure during sputtering was maintained at 2.2 Pa, and the power to the target was 280 W. All the films were prepared at room temperature and sputtering time was 20 mins.

2.2 Electrochemical and optical measurements

The cyclic voltammetry (CV) technique with the different scan rates of 0.05, 0.10 and 0.15 V/s, respectively, are employed to estimate the electrochemical properties and electrochromic performances of the films. For the CV test, the current flow is zero and the voltage corresponding to this zero current is defined as the OCP. Under a work pattern of time scan which can record the relationship between transmittance and time, the time dependence of transmittance of WO_3 films at 550 nm can be in suit recorded upon cycling by ultraviolet–visible–near-infrared spectrophotometer (Shimadzu UV-3101PC) during all electrochemical cycling. Electrochemical tests were performed on a Princeton VersaSTAT 4 electrochemical workstation. The WO_3 films were subjected to electrochemical ion insertion/ extraction in a three electrodes cell with Platinum plate (Pt) as the counter electrode, Ag/AgCl as the reference electrode, and 1 M $LiClO_4$ prepared by lithium perchlorate dissolving into propylene carbonate as the electrolyte.

3. RESULTS AND DISCUSSION

As a useful tool, the cyclic voltammetry (CV) technique has been frequently employed to estimate the electrochemical properties and electrochromic performances of the films. Specifically, the activity of electrochemical reaction, charge density of inserted ions and electrochromic efficiency etc. of electrochromic films can be simply obtained by CV technique[15, 16]. Nevertheless, more mechanism analysis for electrochromic films is not sufficient by CV test, and especially, there is no unambiguous interpretation for the various cyclic life of film under different test conditions. In this study, we will innovatively exhibit the extraordinary role of CV technique in analyzing the performances of electrochromic films. During CV test, by setting the different scan rates of 0.05, 0.10 and 0.15 V/s, the electrochromic WO_3 films will exhibit various the ion behaviors, and the CV curves of the WO_3 films are shown in Fig. 1(a), and the applied potential window is taken in the range of -1 V and 0.8 V. The current density of anodic peak (I_p) is 1.68 mA cm^{-2}, 2.42 mA cm^{-2} and 2.76 mA cm^{-2} for the different scan rates of 0.05, 0.10 and 0.15 V/s, respectively, and the plot of the peak current I_p as a function of square root of scan rate is given in the inset of Fig. 1(a). For an reversible system (rapid and reversible transport of ions on the electrode surface), the peak current is described by the Randles-Sevcik equation,[17] and the better linear nature between peak current I_p and square root of

scan rates $v^{1/2}$ confirms a ion diffusion-controlled behavior for the redox reaction.[18] In addition, the charge density of inserted ion and extracted ion can be calculated by the integration of CV curves, which complies the following equation:[19]

$$Q = \frac{\int I \, dV}{v} \qquad (2)$$

The charge density of different test parameters are calculated and shown in Fig. 1(b). The inserted charge density and extracted charge density are calculated from the integration of negative CV curves and positive CV curves, respectively, and the charge density is dependent on not only the CV curve area but scan rate. Although the CV curve area of 0.15 V/s is larger than others, its scan rate is also higher than that of 0.10 V/s and 0.05 V/s. The inserted charge density calculated by equation (2) is 29.70 mC cm^{-2}, 24.06 mC cm^{-2} and 17.74 mC cm^{-2} for the films of 0.05 V/s, 0.10 V/s and 0.15 V/s, respectively. In addition, we can clearly find that there is obvious difference between inserted charge and extracted charge as shown in Fig. 1(b), which means that a part of inserted ions can not be extracted from the film. These ions are defined as trapped ions, and Fig. 1(c) exhibits the relationship between the charge density of trapped ions and scan rates, which demonstrates that the slow scan rate will cause the forming of more trapped ions in film during CV test.
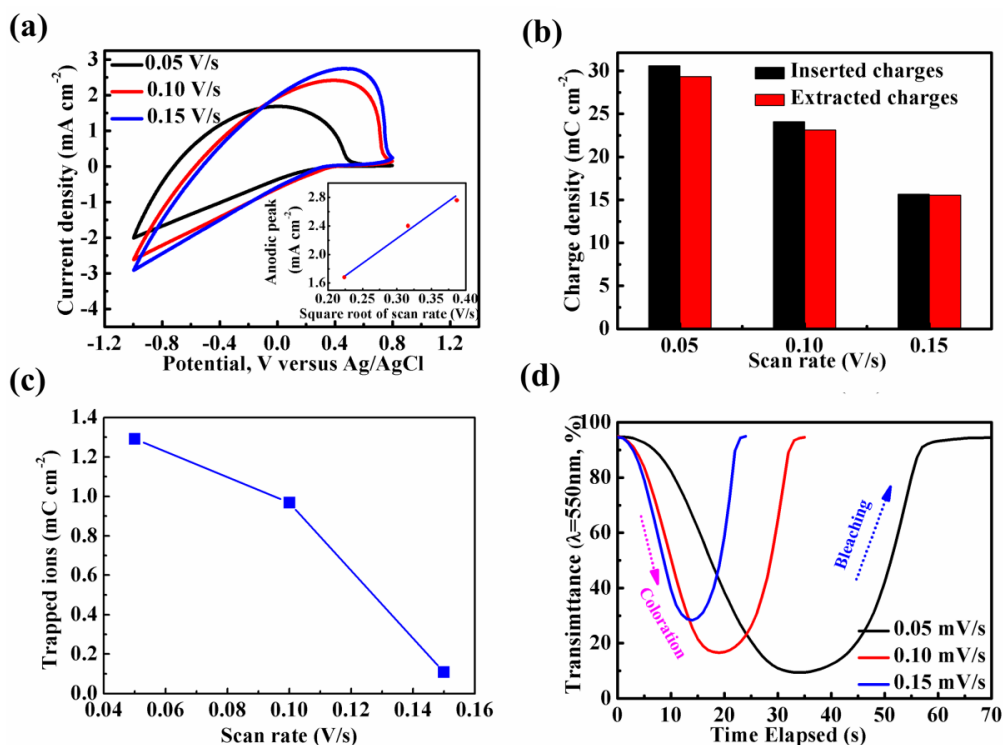

Figure 1. Electrochemical properties and electrochromic performances of the WO$_3$ film under different scan rates by CV test. (a) CV curves. (b) The charge density of the inserted ions and extracted ions. (c) The relationship between trapped ions and scan rates. (d) In-situ transmittance of the film at the wavelength of 550 nm.

In each cycle, the insertion of ions results in the change of the WO$_3$ film from colorless to blue and vice versa. The charge density of inserted ions is consistent with optical modulation ability of film,

and Fig. 1(d) gives the in-situ transmittance of film at the wavelength of 550 nm. The film under the slowest scan rate of 0.05 V/s has the deepest coloration transmittance of 8.96% and the largest optical modulation ability (the difference of transmittances between the bleaching and coloration states) of 85.74%. By the same way, the coloration transmittance of the WO$_3$ film under 0.10 V/s and 0.15 V/s is 16.67% and 28.37%, respectively. These results demonstrate that during CV test, , the film exhibits various ion storage and optical modulation ability under different scan rates.

The electrohromic performances of the WO$_3$ film usually suffer the degradation when the trapped ions form in the host structure. However, the detail is still unknown and especially, it lacks direct study for the mechanism of tapped ions eroding the optical modulation ability of WO$_3$ film. The above results have demonstrated that the charge density of trapped ions in WO$_3$ film is affected by the scan rate during CV test. It is interesting to study the cyclic stability of the film under different scan rates. As shown in Fig. 2(a), the WO$_3$ film tested at 0.05 V/s exhibits rapid degradation during original 900 cycles and no obvious decay from the 900 to 3000 cycle.
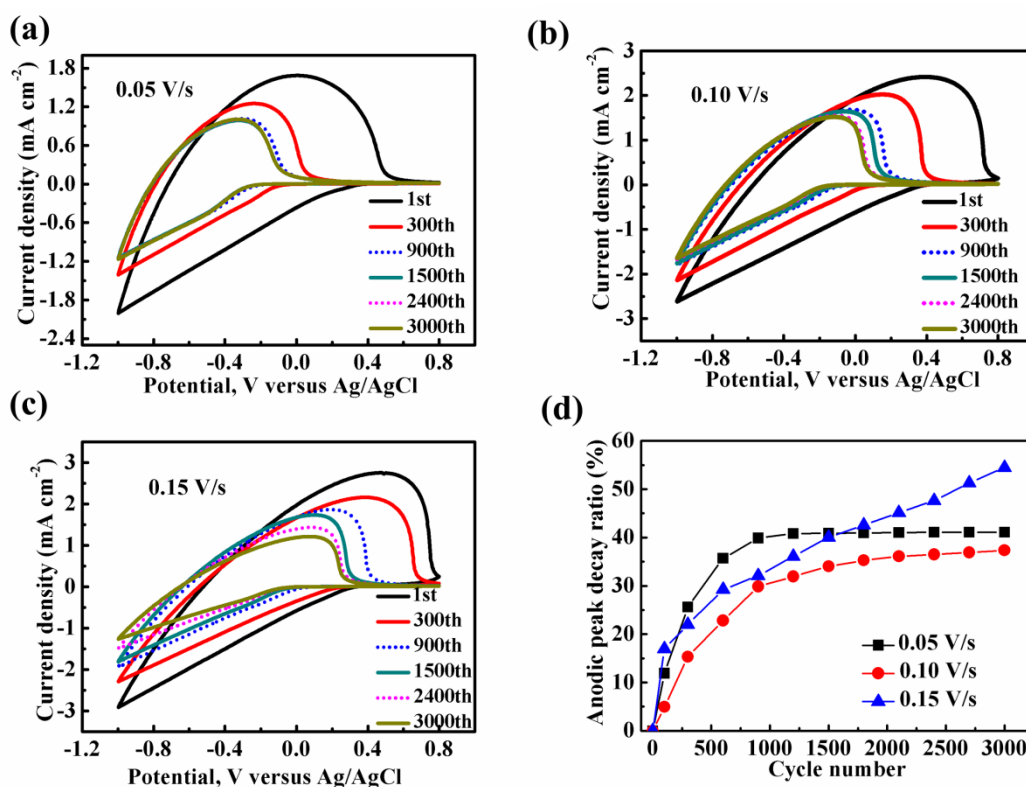

Figure 2. the CV evolutions of film at various scan rates: (a) 0.05 V/s, (b) 0.10 V/s, (c) 0.15 V/s; and (d) the decay ratio of anodic peak current of film under different scan rates.

When the scan rate increases to 0.10 V/s, the cyclic stability decreases rapidly during original 900 cycles and then shows weak decay between 900th and 3000th cycles (Fig. 2(b)). When the scan rate is further increased to 0.15 V/s, the peak current density exhibits a maximal value at the initial cycle, and then gradually degrades upon cycling during total 3000 cycles (Fig. 2(c)). The stability under different scan rates can be more accurately compared by the evolution of decay ratios (R_{pa}) of anodic peak current density which can be obtained by the following equation:

$$R_{pa} = (1 - \frac{I_n}{I_o}) \times 100\% \qquad (3)$$

where I_o and I_n are current density of anodic peak of film at the original cycle and the n cycle, respectively. As shown in Fig. 2(d), the peak current density of 0.05 V/s decreases by 41% after 900 cycles and then remains stable. For the 0.15 V/s, the decay ratio is 41% after about 1600 cycles and then reachs to 55% after 3000 cycles and exhibits serious degradation. On the contrary, the film under 0.10 V/s only decreases by 36% after 3000th cycle and exhibits the least decay ratio.
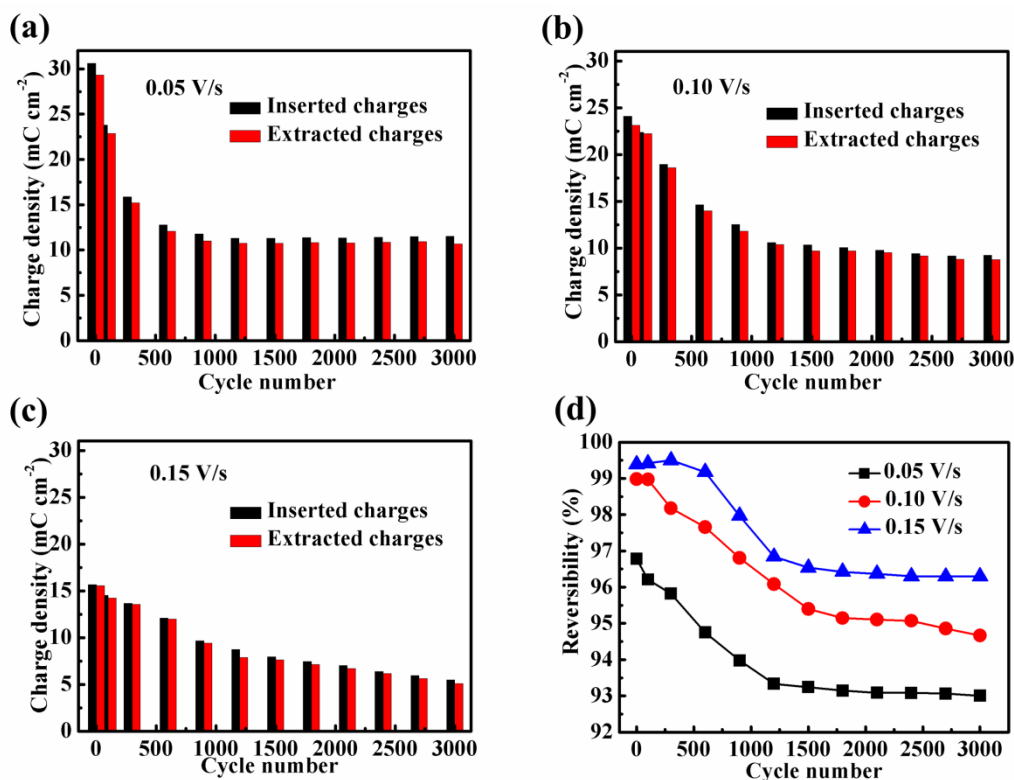

Figure 3. Evolution of the charge density of inserted ions in the WO$_3$ film under different scan rates with (a) 0.05 V/s, (b) 0.10 V/s, (c) 0.15 V/s; and (d) the evolution of the reversibility between inserted ions and extracted ions.

According to equation (2), the evolution of charge density of inserted ions can be calculated. As shown in Fig. 3, the relationship between stability of charge density and scan rate is consistent with CV evolution. In addition, from the Fig. 3(a-c), there is a part of irreversible ions accumulating in film which is equal to the difference between amount of the inserted ions and extracted ions as above mentioned. Usually, the film with high durability is required to prohibit the accumulation of inserted ions in the electrochromic film. As above mentioned, the forming of the accumulated ions is due to that the inserted ions are trapped in host structure and can not extracted in the subsequent bleaching process. So these ions are also called as "trapped ions", and the "m" cycle, the amount of the trapped ions (Q_{trap}) at can be calculated as following:[20]

$$Q_{trap} = \int_1^m \{(1 - R) \times Q_{in}\} \, dn \qquad (4)$$

where Q_{in} is the amount of inserted ions, R is the ion reversibility expressed as the ratio of extracted ions (Q_{ex}) to inserted ions (Q_{in}) [21] between the *1* and *m* cycles. The Q_{trap} is dependent on the amount of inserted ions Q_{in} and the reversibility R. As shown in the Fig. 3(d), the R of slow scan is lower than that of high scan rate at the same cycle, and the amount of inserted ions (Q_{in}) of low scan rate is more than that of high scan rate. Consequently, the total amount of "trapped ions" in film calculated by the equation (4) increases with the lowering of scan rate.
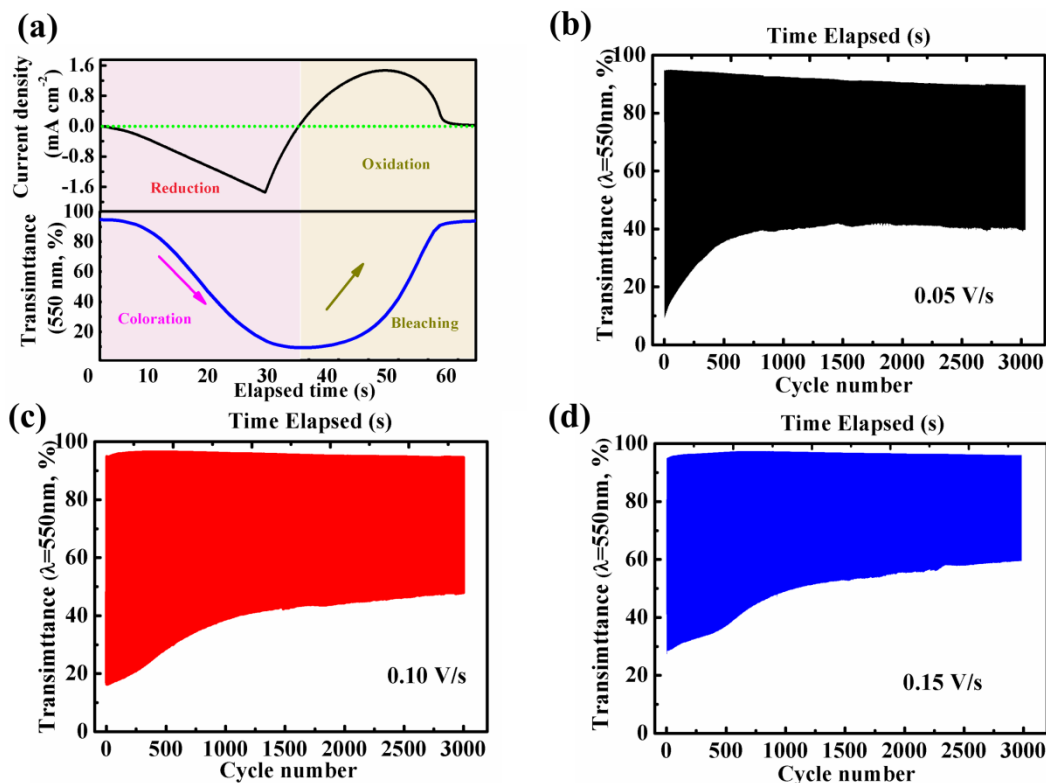
Figure 4. (a) In-situ observation of the transmittance at λ=550 nm under CV test of scan rate 0.05 V/s, and the cyclic evolution of the optical transmittance at λ=550 nm for the WO₃ film under different scan rates of (b) 0.05 V/s, (c) 0.10 V/s and (d) 0.15 V/s.

The color of the WO₃ film will be changed from colorless to blue when the ions are inserted into the host structure. The in-situ measurement of optical transmittance of the WO₃ film at λ=550 nm is synchronously recorded during CV measurements, and as an example, the scan rate of 0.05 V/s is shown in Fig. 4(a). A downward transmittance curve and negative current response are obtained when the potential sweeps from 0.38 V to -1.00 V then returning to -0.72 V, which corresponds to the coloration process. In the bleaching process, an upward transmittance curve and positive current response can also be found when the potential sweeps from -0.72 V to 0.80 V then returning to 0.38 V. The in-situ optical transmittances of 0.10 V/s and 0.15 V/s are recorded by the same method. The optical performances are shown in Fig. 4(b-d), and the degradations of coloration state are more serious than bleaching for all scan rates. Especially, for the film under the scan rate of 0.10 V/s and 0.15 V/s, the optical degradation mainly comes from the attenuation of the coloration transmittance, and the bleaching state almost keeps no obvious decay during all cycles as shown in Fig. 4(c) and 4(d).

For the 0.05 V/s, although the transmittance of film at bleaching state shows slight decay, the degradation of coloration state is more obvious (Fig. 4(b)).

These results demonstrate that the degradation of electrochromic performances is mainly due to the decay of coloration state. The weak decay of bleaching transmittance can be attributed the forming of trapped ions as above mentioned [20]. However, the mechanism of degradation of coloration state is still unknown. According to the equation (1), the coloration process is correspond to the ion insertion reaction: $WO_3 + x(Li^+ + e^-) \rightarrow Li_xWO_3$, and the response of transmittance during coloration process is due to the forming of W^{5+} color centers by inserting Li^+ ions into the WO_3 host structure.[1] Obviously, the decay of coloration state is correspond to the decrease of the quantity of color centers during the coloration reaction. Combining with the data of charge density evolution of different scan rates as shown in Fig. 3(a), (b), (c), it can be determined that the decrease of the amount of color centers and the degradation of coloration transmittance are related with the decay of the charge density of inserted ions. In this case, it is key point to explain the degradation mechanism of electrochromic WO_3 film by exploring the reason of the decrease of the inserted ions.

The open-circuit-potential (OCP) measurement is an efficient and suitable tool for quality assessment of modified electrode and electrochemical system[22]. Evaluating the durability of film electrodes by employing OCP can be performed in significantly shorter times than those needed to complete long-term exposure tests[23]. Experimental set-ups are designed to attain an equilibrium situation, where all anodic and cathodic reactions proceed at an equal finite rate. Consequently, the current flow is zero and the voltage corresponding to this zero current is defined as the OCP, and the electrochemical properties of electrode materials can be obtained by the OCP. As shown in Fig. 5(a), at the bleaching state, the electrochemical system remains equilibrium situation, and the Li^+ ions cannot spontaneously diffuse into the WO_3 film. During CV test, a linear potential (E) applied on the electrodes sweeps from positive potential of +0.8 V to negative potential -1 V then returns to +0.8 V by the scan rate of 0.05 V/s, as shown in Fig. 5(b). Here, the direction of E sweeping from +0.8 V to -1 V has been defined as negative direction, and that of E sweeping from -1 V returning to +0.8 V is called as positive direction[24, 25]. In negative scan direction, when the response current density is zero, the potential corresponding to this zero current is marked as E_1 which is equal to OCP of WO_3 film at bleaching state. When E is more negative than OCP, the negative current density is produced and the ions begin to be inserted into the film, which corresponds to the coloration process. These results demonstrate that the electric field force used to drive ions into film is dependent on the relative intensity of E to OCP in the negative direction, and specifically, the more negative potential of E relative to OCP will produce the stronger ion driving force during coloration process. In the positive scan, when the current density is equal to zero, the sweep potential corresponding to this zero current is marked as $E=E_2$, and at this moment, the amount of inserted ions in film has reached to the maximum value, which is correspondent to the full coloration state of film as shown in the below chart of Fig. 5(a). By the same way, when the potential E is more positive than E_2 in the positive direction, the ions will be extracted from the film and cause the change from coloration to bleaching state. It is worth noting that in the all test of this study, the value of OCP is defined and obtained by always setting the work electrode of WO_3 film at bleaching state as positive electrode and Pt plate as negative electrode. In this case, the OCP is always equal to the relative potential of WO_3 film to Pt plate. When the

residual inserted ions cannot be completely extracted from the WO_3 film, the electrode potential of WO_3 film at bleaching state will shift to more negative than its initial potential. Consequently, the value of OCP may be negative, which is different from the concept of OCP in battery field.
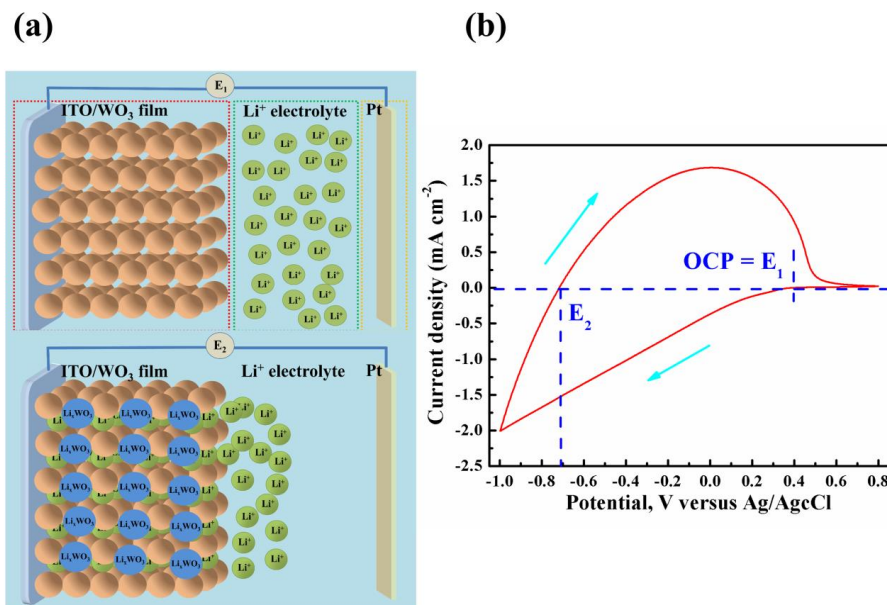
Figure 5. (a) The schematic diagram of OCP during ion insertion process. (b) The calculation method of OCP in CV test.
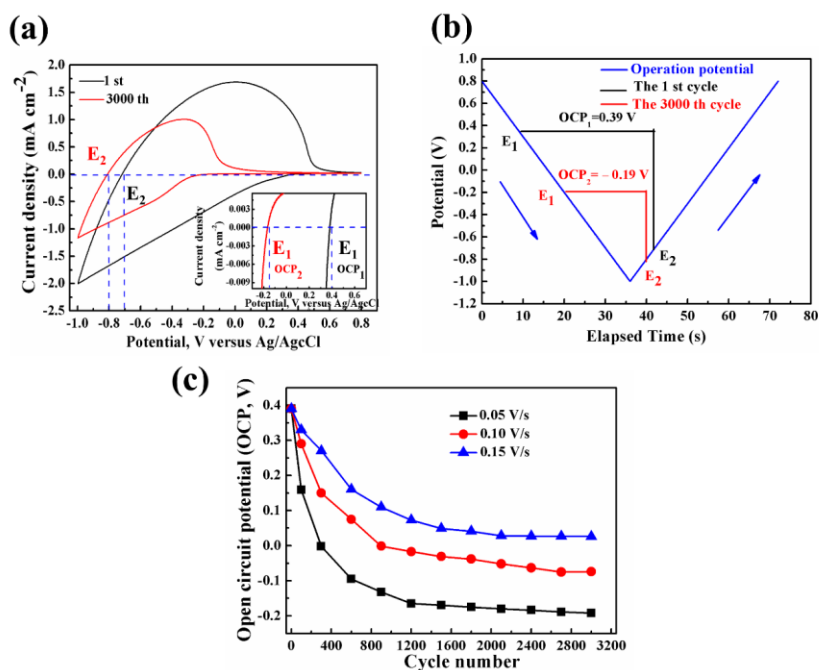

Figure 6. (a) The CV curves of different cycles for the film under the test conditions of 0.05 V/s, and the insert figure gives the change of OCP under different cycles. (b) Under the scan rate of 0.05 V/s, the relative intensity of operation potential E to OCP and coloration range of film at the first and the 3000 cycle, respectively. (c) The evolution of open circuit potential (OCP) of WO_3 film at bleaching during 3000 cycles.

The OCP of the film under scan rate of 0.05 V/s at the first cycle and the 3000 cycle are shown in Fig. 6(a). It is found that the OCP of WO_3 film at bleaching state shifts to the more negative potential after 3000 cycles from an initial value of $OCP_1=0.39$ V to $OCP_2= -0.19$ V. The more negative potential of OCP after repeated cycling is due to the accumulation of the trapped ions in the film and the forming of new chemical species containing elemental lithium in the WO_3 host structure[26].

For the WO_3 film, the coloration behavior is due to the ion insertion process in the host structure, and the driving force for Li^+ transport is electric field force. The behavior of ion transport is dependent on the direction, intensity and duration time of the electric field force. The electric field force used to drive ions into film is dependent on the relative intensity of operation potential E to OCP in negative direction as shown in Fig. 6(b). With the increase of amount of trapped Li^+ ions in WO_3 host structure, the value of OCP will shift to more negative upon cycling. However, the external operation potential applied on the WO_3 work electrode by the electrochemical instrument keep unchanged during whole cycles. Consequently, the relative intensity of the operation potential to OCP in negative direction will be weakened, and the electric force used to drive ions into the film will also gradually be weakened.

In addition, the duration time of the ion insertion process can be accurately obtained by the data of CV test. Taking the film of 0.05 V/s as an example, as shown in Fig. 6(b), the ion inserted process corresponds to the negative current response and the potential range of operation potential E sweeping from E_1 to E_2, and the arrow indicates the direction of potential sweep. At the initial cycle, the coloration process begins from $OCP_1=E_1=0.39$ V to -1 V then returns to $E_2=-0.72$, and the coloration time calculated by the ratio of potential range to scan rate of 0.05 V/s is 33 seconds. After 3000 cycles, the OCP shifts to the more negative value of -0.19 V, and the range of coloration potential is begins from $OCP_2=E_1= -0.19$ V to -1 V and finally returns to $E_2=-0.80$ V. Consequently, the time of ion insertion process is shortened to 27 s. These results show that the more negative potential of OCP can cause the decrease of coloration potential range and the duration time of ion insertion process. Moreover, the evolutions of OCP of WO_3 film under different scan rates during 3000 cycles are shown in Fig. 6(c). OCP evolution of film under 0.10 V/s and 0.15 V/s have the similar trend to that of 0.05 V/s, and specifically, the OCP shifts from an initial value of 0.39 V to -0.074 V and 0.026 V for the sample of 0.10 V/s and 0.15 V/s after 3000 cycles, respectively. The degree of change of OCP is dependent on the amount of trapped ions in film, and as above mentioned, the slowest scan rate of 0.05 V/s has produced the most trapped ions. Consequently, the OCP of the film under the scan rate of 0.05 V/s shows the most obvious change as shown in Fig. 6(c).

The effect of the OCP on charge density of inserted ions can be shown by the schematic diagram in Fig. 7. It demonstrates that the decay of OCP of film at bleaching state is due to the forming of microquantity trapped ions in the structure. In the ion insertion process, the decay of OCP not only weakens the electric field intensity used to drive ions into the film, but shortens the duration time of the force. As a result, the amount of the ions inserted into WO_3 host structure will decline with cycling, and the coloration transmittance of film will exhibit seriously degradation after repeated cycling, which is the main factor of causing the degradation of cyclic life of WO_3 film. This study offers us a new tool to study and understand the degradation of electrochromic materials.
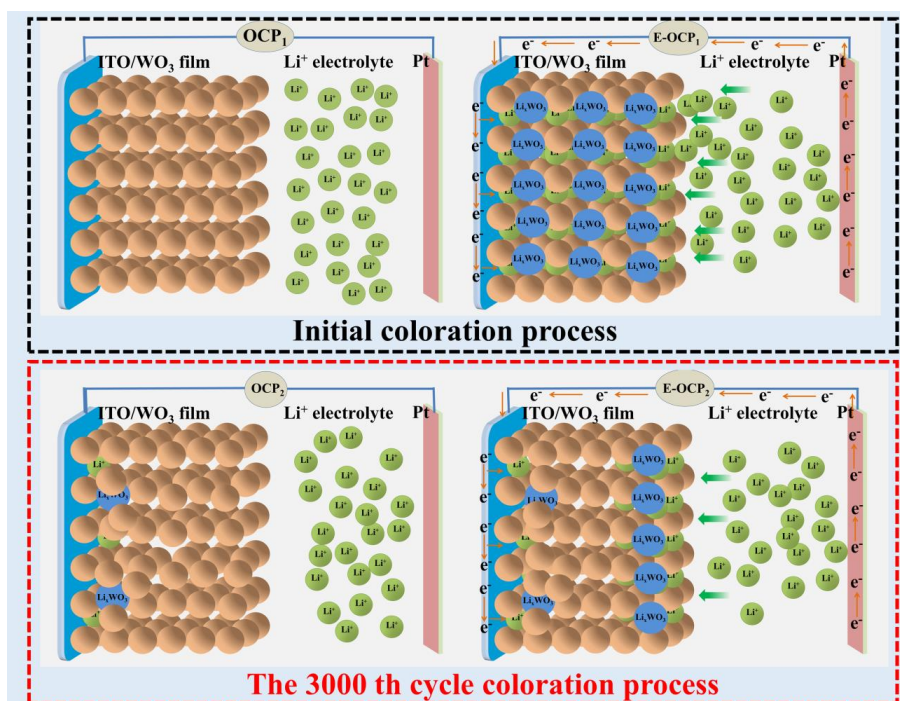
Figure 7. Schematic diagram of the effect of trapped ions on the OCP and charge density of inserted ions.

4. CONCLUSION

The long-term electrochromic performances of WO_3 devices are normally mainly subject to the effect of trapped ions in the host structure. In this study, we found that more trapped ions will accumulate in the host material with the increasing of charge density of inserted ions during CV test, which will result in the decline of optical modulation ability by the decay of bleaching state and coloration state. Notably, the forming of trapped ions in host structure will cause the obviously decay of coloration state, which is the main factor of effecting the optical modulation of the electrochromic WO_3 film. This study demonstrates that the decay of coloration state is attributed to the decrease of the charge density of inserted ions in the film. By employing the open circuit potential (OCP) measurement, the trapped ions in host structure will decay the OCP which consists of WO_3 film and reference electrode. The decay of OCP will weaken the electric field force used to drive ions into the film and shorten the duration time of the force. As a result, the amount of ions inserted into WO_3 host structure will decline with cycling, and the coloration transmittance of film will exhibit seriously degradation after repeated cycling, which is the main factor of causing the degradation of WO_3 film. This study will correct the inaccurate understand of the degradation of WO_3 film and offers us a new tool to study and understand the degradation of the electrochromic materials. Finally, the work has also further implications for lithium ion batteries, supercapacitors and other types of ionics-based materials.

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