

Effects of electrolyte solutions and their pH on the electrochromic cycling stability of reactively sputtered WO₃ thin films

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WO₃ thin films are well known electrochromic (EC) materials due to its brilliant EC properties. Typically EC devices are composed of a first transparent conductive oxide (TCO) layer, an EC layer, an ion conductor, an ion storage layer and a second TCO layer. While complementary EC devices have two EC layers, cathodically colouring layer (e.g. WO₃) as the first EC layer and anodically colouring layer (e.g. NiOOH) as the second EC layer and the ion storage layer, and these devices exhibit high EC performance. However, WO₃ and NiOOH are inconsistent in chemical properties. NiOOH is stable in basic solutions, while WO₃ is rather stable in acidic solutions. In our previous study, WO₃ thin films prepared at a substrate temperature of 200 °C exhibited stable durability and good EC properties. The purpose of this study is to investigate the effects of electrolyte solutions on the EC cycling stability of the WO₃ thin films.

WO₃ thin films were prepared onto TCO-coated glass substrates using reactive R.F. magnetron sputtering process. W target was sputtered in oxygen atmosphere and WO₃ films were deposited at a substrate temperature of 200 °C. In this study, all the films were approximately 100 nm thick. Prepared WO₃ thin films were cycled in acidic and neutral electrolytes in the pH range of 0-6 using H₂SO₄, K₂SO₄, Na₂SO₄, H₂SO₄+K₂SO₄ and H₂SO₄+Na₂SO₄ aqueous solutions. K₂SO₄ and Na₂SO₄ were added as supporting electrolytes to maintain a constant conductivity of the electrolytes (approximately 10 S/m).

Figure 1 shows the transmittance change of the WO₃ thin films during cycling up to 100 cycles in different aqueous electrolytes. A stable and good EC cycling was obtained in the weak acidic solution (pH 3). Nearly the same results were observed at pH 4. In strong acidic solution (pH 0), the WO₃ thin films exhibited high transmittance change at early cycles. However, it dissolved rapidly after 50th cycle. In this pH region, WO₃ was dissolved and formed cationic species [1]. In neutral solution (pH 6), the WO₃ thin films exhibited quite little transmittance change even at early cycles and it showed no transmittance change after 20th cycle.

Cyclic voltammograms (CV) at 5th and 100th cycle of the WO₃ thin films cycled in different electrolytes are shown in Figure 2. In weak acidic solution (pH 3), a stable CV curve was obtained up to 100 cycles. In strong acidic solution (pH 0), although large current (transfer charge) was observed at early cycles, it became much smaller at 100th cycle due to the dissolution of the WO₃ thin films. In neutral solution, the WO₃ thin films hardly showed redox reactions. In the H₂SO₄+K₂SO₄ solutions, the EC properties of the WO₃ thin films degraded faster than the films cycled in the H₂SO₄+Na₂SO₄ solutions.

These results showed WO₃ thin films prepared at substrate temperature of 200 °C exhibited good EC cycling stability during 100 cycles in weak acidic electrolyte solutions of pH 3-4. In strong acidic and neutral electrolyte solutions, however, the WO₃ thin films were

dissolved and their EC performance was degraded only after several tenth of cycles.

Reference

[1] S. Sun, P.H. Holloway, *J. Vac. Sci. Technol.*, vol. 1, n. 2, p.529 (1983)

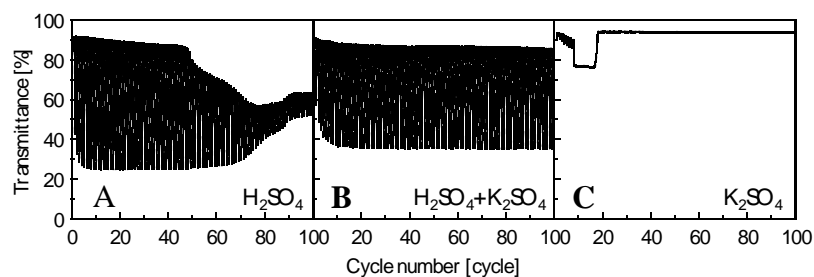


Fig. 1. EC cycling stabilities of WO₃ thin films in (A) strong acidic (H₂SO₄, pH 0), (B) weak acidic (H₂SO₄+K₂SO₄, pH 3) and (C) neutral (K₂SO₄, pH 6) electrolytes.

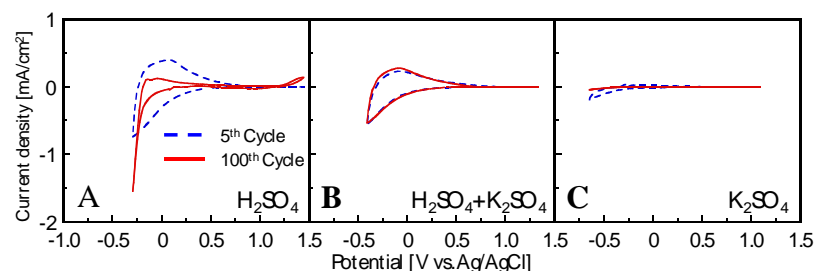


Fig. 2. Cyclic voltammograms of WO₃ thin films in (A) strong acidic (H₂SO₄, pH 0), (B) weak acidic (H₂SO₄+K₂SO₄, pH 3) and (C) neutral (K₂SO₄, pH 6) electrolytes.