## ELECTROCHROMIC PROPERTIES OF LITHIUM FLEXIBLE DEVICES BASED ON TUNGSTEN AND VANADIUM-TITANIUM OXIDE THIN FILMS MARCEL C., VINCENT A., BRIGOULEIX C., NOUHAUD G., HAMON Y., SABARY F. CEA/Le Ripault BP16, 37260 Monts, FRANCE.

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Typical blue absorption of vanadium oxide, yielding a yellow color, is undesirable for any electrochromic application in the visible spectral domain [1]. Hence the utilization of vanadium based mixed oxides is required to obtain a more neutral coloration. Besides, it is well known that the addition of titanium, cerium or zirconium improves the cyclability and the neutrality of coloration in vanadium oxide thin films [2, 3]. In this frame lithium electrochromic devices were prepared by the lamination of two tungsten and vanadium-titanium oxide thin films deposited by roll-toroll radiofrequence sputtering technique. An ITO-coated mylar substrate was used to realize flexible devices adaptable for an eyewear application. Tungsten oxide was set as the working electrode, while vanadium-titanium oxide mixtures were examined as counter-electrodes. The electrolyte used to assemble both electrodes was a polymer gel lithium ionic conductor constituted of a LiTFSI lithium salt dissolved in PC, and incorporated within a photopolymerized acrylate matrix [4].

Counter-electrode electrochromic properties were investigated for four atomic ratios of titanium varying in the (0-100%) range by step of 25%. A blue shift effect in the transmittance spectra of as-deposited films was first observed as the titanium amount increased (Figure 1). Moreover, the electrochemical capacity and stability upon lithium intercalation was improved with the presence of titanium (Figure 2). In situ optical behavior was investigated while cycling in the (1.5-4V) potential range, and the film containing an equal proportion of vanadium and titanium displayed a remarkable neutrality of coloration (Figure 3).

Complete devices were elaborated with different Ti/V ratios of 0, 1:3, 1:1 and 3:1 in the counter-electrode. While tungsten oxide film thickness was fixed to 300 nm, the thickness of vanadium-titanium oxide films was tuned upon their respective electrochemical capacity. The obtained electrochromic performances combined with their cycling lifetime and response time will assess the choice of vanadium-titanium proportions.

## **References:**

[1] C.G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, p. 323, Elsevier, Amsterdam (1995).

[2] A. Surca, S. Bencic, B. Orel and B. Pikhar, *Electrochimica Acta*, 44, 3075 (1999).

[3] E. Masetti, F. Varsano and F. Decker, *Electrochimica Acta*, **44**, 3117 (1999).

[4] B. Claude-Montigny, E. Rioteau, D. Lemordant, P. Topart, G. Bosser, *Electrochimica Acta*, **47**, 533 (2001).



Fig. 1. Optical behavior of as-deposited V-Ti mixed oxide counter-electrodes in the following Ti/V ratios:
1) 100/0; 2)75/25; 3)50/50; 4)25/75; 5) 0/100.



*Fig. 2.* Electrochemical behavior of as-deposited V-Ti mixed oxide counter-electrodes cycled between 1.9 and 3.8 Volts vs. Li<sup>+</sup>/Li, in the following Ti/V ratios: 1) 100/0; 2)75/25; 3)50/50; 4)25/75; 5) 0/100.



*Fig.3.* Evolution of the transmission spectrum of a 100 nm thick counter-electrode (Ti/V=1:1) upon cycling in the (1.5-4V) range vs. Li<sup>+</sup>/Li.