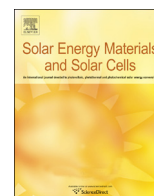




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All inorganic thin film electrochromic device using LiPON as the ion conductor

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ABSTRACT

All inorganic solid-state thin-film electrochromic devices based on lithium ion (Li^+) insertion and using lithium phosphorus oxynitride (LiPON) as the ion conductor were fabricated by physical vapor deposition technology. Multilayer architecture consisting of TCO/ V_2O_5 /LiPON/ Li_xWO_3 /TCO was deposited by RF sputtering technology on glass substrate. Electro-optical characterization carried out on complete devices highlighted transmittance changes as large as 40% at 600 nm wavelength upon ± 1.5 V voltage application, with coloring and bleaching time of 30 s. Several hundreds of bleaching/coloration cycles have been carried out with almost no performance degradation.

The effect of the multilayer architecture was investigated. The results showed interactions between the depositing and the deposited layers, which influences the total amount of injected charges and hence the device performance. In particular, it has been observed a reversibly inserted Li^+ charge capacity during LiPON deposition and a charge capacity extraction during deposition in presence of lithiated layers. The described phenomena should be considered in order to achieve the charge balance between the electrodes for optimum device performance.

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1. Introduction

Over the past few decades, electrochromic devices have attracted increasing attention because of their interesting characteristics such as high coloration efficiency, low power consumption and open circuit memory in either the bleached or the colored state.

Electrochromic devices have many potential applications such as smart windows, switchable mirrors, information displays and variable emittance infrared skins [1–6]. Durability is an important property for many of the aforementioned applications. Among all device configurations, lithium ion (Li^+) based all inorganic thin film structures may present considerable advantages regarding physical and electrical durability [7,8].

An inorganic all thin film electrochromic device consists of a substrate on which are deposited successively a first transparent conductor, a first electrochromic layer, an ion conducting layer, a second electrochromic layer and a second transparent conductor. For Li^+ based devices, the ion conducting layer is a thin film material which allows rapid transfer of Li^+ between

electrochromic layers without transporting electrons between them. Therefore, the ion conducting layer should have a relatively high Li^+ conductivity ($\geq 10^{-7} \text{ S cm}^{-1}$ at room temperature) and relatively low electronic conductivity ($\leq 10^{-12} \text{ S cm}^{-1}$ at room temperature). Moreover, the ion conducting layer should have a high optical transmittance in the considered spectral range.

Table 1 covers selected works on reported results for Li^+ based all thin film inorganic electrochromic devices integrating different ion conducting layers [9–18].

Most of the ion conducting materials listed in Table 1 present useful ionic and electronic conductivities for electrochromic applications, yet with limitations regarding stability issues for some of them. For example, Oi et al. [19] reported on the degradation of LiAlF_4 film conductivity (and more generally on evaporated mLiF.nAlF_3 layers) as an effect of temperature and humidity variation. Ito et al. reported the hygroscopic nature of evaporated lithium borate thin films with different compositions [20]. It was also reported that lithium sulfur-containing ion conductors were highly hygroscopic and were difficult to fabricate because of their corrosive nature [21].

Lithium phosphorus oxynitride (LiPON) is an inorganic lithium ion conductor film which present high electrochemical and physical stability [22]. LiPON has been widely investigated for use as ion conductor in thin film batteries devices; however, not much

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Table 1
Selected Li⁺ all thin film inorganic electrochromic devices.

Electrochromic materials	Ionic conducting layer			Ref.	
	Material	Thickness(nm)	Li ⁺ conductivity(S cm ⁻¹ , rT)		Electronic conductivity(S cm ⁻¹ , rT)
WO ₃ /V ₂ O ₅	LiNbO ₃	–	1 × 10 ⁻⁷	1 × 10 ⁻¹¹	[9]
WO ₃ /LiCoO ₂	LiNbO ₃	450	–	–	[10]
Li _x V ₂ O ₅ /WO ₃	LiBO ₂	1000	6 × 10 ⁻⁸	1 × 10 ⁻¹²	[11]
LiNiO _x /WO ₃	Li _x TaO _y	170	3.3 × 10 ⁻⁷	–	[12]
Li ₂ Li _y CrO _{2+x} /WO ₃	Li ₂ O–B ₂ O ₃	320	1 × 10 ⁻⁹	–	[13]
WO ₃ /V ₂ O ₅	LiAlF ₄	800	–	–	[14]
WO ₃ /NiO	LiNbO ₃	980	2 × 10 ⁻⁷	2 × 10 ⁻¹¹	[15]
WO ₃ /LiCoO ₂	LiPON	1600	–	–	[16]
MoO ₃ /NiO _x	LiBO ₂ –Li ₂ SO ₄	300	–	–	[17]
NiO _x /WO ₃	LiBO ₂ –Li ₂ SO ₄	300	–	–	[18]

(–): Not available data.

work has been published on its optical and electrical properties for electrochromic applications [16,23,24].

In this work, we fabricated all inorganic solid-state thin-film electrochromic devices using LiPON as ion conductor and presenting different multilayer architectures.

2. Experimental

All film depositions were carried out in an Alcatel SCM600 tool equipped with three sputtering targets and a thermal evaporation source. The tool was connected to an Ar filled glove box in order to control the sample transfer and storage atmosphere. 4 × 4 cm² Pre-cleaned Indium Tin Oxide (ITO, 30 Ω/□ sheet resistance) coated glass slides were used as substrates. Amorphous tungsten oxide WO₃, vanadium oxide V₂O₅ and lithium phosphorus oxynitride LiPON were prepared by reactive magnetron sputtering. Depending on the device architecture, lithium insertion was carried out (either in V₂O₅ or WO₃) through a dry lithiation method by exposing the film in vacuum to Li vapor atoms, which were given off by thermal evaporation of a Li foil. The evaporated lithium thickness was measured by quartz crystal technique. The details of all deposition conditions are listed in Table 1.

Films of WO₃ and V₂O₅ were deposited on glass/ITO substrate by sputtering and were characterized by XRD using a diffractometer (D8 advance, Bruker AXS) of Cu-Kα₁ incident radiation (λ = 1.54056 Å). The cross-sectional morphology of the electrochromic device multilayer was observed by SEM (Helios nanolab 450S dual beam FIB/SEM, FEI). The optical transmittance of glass/ITO/LiPON samples was measured over the wavelength range from 200 nm to 2000 nm using a spectrophotometer (PerkinElmer lambda 950) with an incident angle of 8°. LiPON ionic and electronic conductivities were obtained respectively from PEIS and CA measurements of glass/ITO/LiPON/Ti structures. Electrochromic devices were put into the spectrophotometer and simultaneously connected to a potentiostat/galvanostat (VMP3, Bio-Logic); the devices were subjected to coloration/bleaching cycling using GCPL and CA techniques. The electrical and optical recordings were done in situ: transmittance was taken at a certain Li⁺ intercalation level without removing the applied current or potential. For long-term cycling studies, the electrochromic devices were hermetically sealed under Argon atmosphere (in a stainless steel cell with a glass window facing the electrochromic active switching area) before being placed in the spectrophotometer.

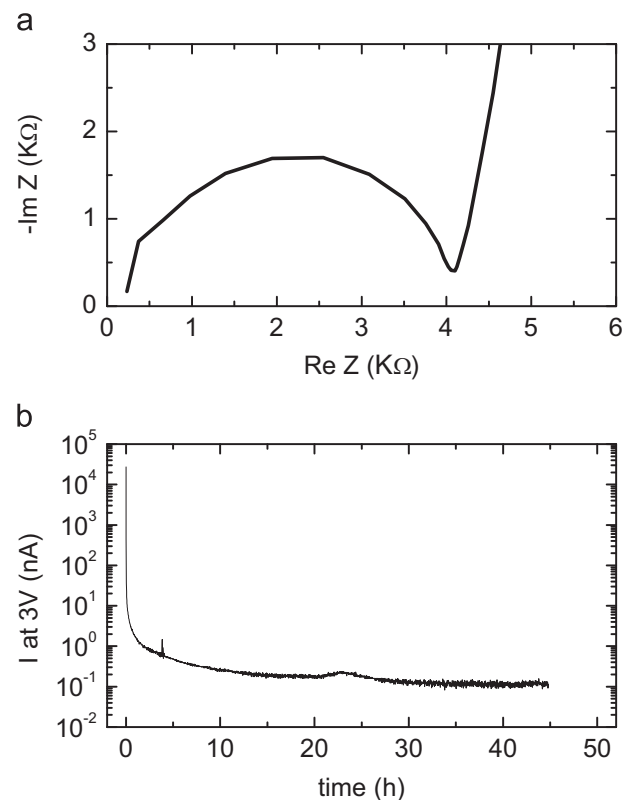


Fig. 1. Electrochemical characterization of glass/ITO/LiPON/Ti cell with an active electrode area of 2.5 mm² at 25 °C: (a) Nyquist plot of PEIS data and (b) time dependence of current during 3 V CA step.

3. Results and discussion

Fig. 1 shows the results of electrochemical characterization of glass/ITO/LiPON/Ti structure fabricated with a LiPON thickness of 1500 nm. Nyquist plot of PEIS data shown in Fig. 1a consists of a depressed semicircle and an almost linear segment, respectively at the high frequency range and the low frequency range. The semicircle is attributed to the impedance response from LiPON film whereas the low frequency segment is attributed to LiPON/electrode interfaces. The PEIS spectrum was fitted with an equivalent circuit model. The ionic conductivity σ_i of LiPON film is calculated based on ion conductor resistance R_{ic} obtained from impedance data fitting, following the relation $\sigma_i = d/(R_{ic} \cdot A)$ where d is LiPON thickness and A is the electrode active area. The ionic conductivity deduced from Fig. 1a is $\sigma_i = 2.7 \times 10^{-6}$ S cm⁻¹. The time dependence of current at

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