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Comments on the Mechanism of Aging of Antimony Doped Tin Oxide Based Electrochromic Devices

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Electrochromic effects of antimony doped tin oxide (ATO) nanoparticles are investigated to probe device yellowing (degradation). Voltage vs contrast ratio curves exhibit hysteresis, i.e., image-sticking phenomena due to irreversible charge insertion. X-ray, impedance and optical b* studies suggest that the yellowing/charge trapping is nanoparticle size-dependent with 4 nm size particles exhibiting the least yellowing. Yellowing results in increased impedances of electrode-electrolyte interface and electrode corrosion. Plausible sources of discoloration are formation of insulating complex alkali oxide film, carrier inversion (n-to-p type) through electrochemical Li doping, redeposition of the corroded electrode material and perhaps residual concentration of charge-transfer species.

KEYWORDS: antimony doped tin oxide (ATO), nanoparticles, electrochromism (EC), charge trapping, X-ray diffraction, electrochemical impedance, EC device degradation

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Non-stoichiometric SnO_x is a rare transparent semiconductor exhibiting a large band-gap (3.6 eV) and high carrier density (10¹⁹-10²¹ cm⁻³)¹. Thin films of SnO_x have been used in applications ranging from electrodes in liquid crystal display devices, solar cells to sensors². Unlike the widely studied WO₃ based electrochromic materials³, the intrinsic electrochromic properties of SnO_x are weak but can be improved by antimony doping. Coleman *et al.* have established an optimum electrochromic performance in antimony doped tin oxide [ATO] when the mole ratio of Sb is 0.42 (= [Sb]/([Sb]+[Sn])) during sol-gel synthesis^{4,5}. Nanocrystalline (casserite lattice) ATO particles (4-9 nm) are readily synthesized by this technique and upon calcination at 600°C the yellow powder transforms to a bluish color due to the presence of free electron carriers at room temperature. The conductivity exhibits a maximum at a doping level of about 5-10 atomic percent⁶, which has been attributed to various mechanisms⁷⁻⁹. The Sb doping leads to n-type conductivity by creating delocalized donor atom states near the conduction band of SnO_x. Materials and device optimization for flexible and inexpensive displays exploiting novel *in-plane* anode-cathode configurations have been elucidated in a series of papers^{4,5}. The electrochromic (EC) devices exhibit remarkable (1) memory effect (refresh times~2-24 h), (2) low-power consumption (needing only 10-100 μA/cm²@ 1-1.2 operational voltage) and (3) reasonable contrast ratios (2-4).

The EC devices were constructed on flexible plastic substrates. Screen-printing, anodic and cathodic areas separated by plastic insulation, was achieved by successive deposition of silver paint, carbon ink (to prevent corrosion of Ag), TiO₂ (conductive and reflective particles) followed by an electrochromic layer of ATO nanoparticles (dispersed in Viton, a fluoroelastomer), total electro-active layer thickness ≈ 50 μm. The electrolyte contained 30% LiCl solution in a polymeric gel (see Fig. 1). Upon application of DC voltage, the anodic area

becomes transparent due to carrier depletion and appears white due to light reflection from the underlying TiO₂ layer. In the cathodic region, injection of electrons and migration of Li ions in the electrochromic layer increases its optical absorption and it appears black⁷⁻⁹.

This paper examines factors affecting the device lifetime/aging, specifically the origins of distinct yellowish discoloration observed in the cathodic region during operation. Discoloration increases with the operation time and the magnitude of DC voltage. Bipolar pulse driving scheme (switching electrode polarities) reduces the extent of yellowing ($\propto 1/\text{frequency}$). Given the mixed valence nature of both Sn^{+4/+2} and Sb^{+5/+3} oxides, the development of their colored charge transfer complexes was probed using Sn Mössbauer¹⁰ and Sb X-ray absorption near edge structure (XANES) spectroscopies¹¹. Sn Mössbauer spectra [Fig. 2(a)] from yellowed regions do not show presence of peak(s) at 4-6 mm/sec, characteristic of Sn⁺², neither do the antimony L₁ edge in XANE spectra reveal Sb⁺³ ions [Fig. 2(b)]. X-ray photoelectron spectroscopy studies showed no difference in elemental composition eliminating potential source due to electrolyte/polymer degradation. Treatment with oxidizing (NaOCl) or reducing (SnCl₂) solutions does not alter the discoloration.

Evolution of contrast ratio ($\text{CR} \propto \text{injected charge}$), as the device is slowly (time ≈ 3 h) cycled between positive and negative voltages, exhibits distinct hysteresis [Fig. 3(a)] with non-zero CR at V=0, after voltage cycling. It suggests an impeded movement of ions from nanoparticulate laden electrodes, i.e., irreversibility of $\text{Sb(V)}_2\text{O}_5 + 4\text{e}^- + 4\text{Li}^+ \leftrightarrow \text{Li}_4\text{Sb(III)}_2\text{O}_5$ reaction at cathode, similar to trapping of electrons in Si nanoparticles^{12,13} embedded in transistor gates. To quantify yellowing, we measured b* (CIE 1976 color coordinate) using an Ocean OpticsTM reflection spectrometer, 15 min after shorting anode and cathode together. For fresh and yellowed samples b* values are about 2 and >4, respectively. Figure 3(b) shows

development of b^* as a function of device operation (at 1.2 V) time. b^* exhibits a logarithmic growth, [$b^* \sim \log(t)^{0.5}$]. While experiments involving fixed charging time and variable discharge times yielded a smaller slope of -0.3 . Thus, the electrochromic process appears to be only partially reversible, controlled by very slow kinetics of charge movement.

We employed impedance spectroscopy (from 5 Hz-14 MHz, HP4192 LCR meter interfaced to a PC) to study charge transport processes between the electrolyte-electrode interface. The Nyquist plots (Fig. 4) were analyzed using^{14,15} Randle's equivalent circuit (Zsimp Version 3.2, from Princeton applied research); see Table I. Here R_s , R_p , and C are the high frequency solution resistance, the polarization resistance, and the net capacitance (due electrode-electrolyte double layer and a series capacitance due to depletion layer in the semiconductor) respectively; W is the Warburg impedance. R_p increased (Table I) with the applied potential consistent with Volmer-Butler mechanism^{14,15}. The corresponding decrease in C indicated increased depletion layer thickness⁹. The mildly yellowed samples also showed an increase in R_p , W , and R_s . For deeply yellowed samples, observed (Table I) precipitous rise in R_p and W and drastic decrease in C implied electrode restructuring due to growth of an insulating barrier and electrochemical corrosion.

X-ray diffraction studies of fresh and degraded devices, Fig. 5, indicated that upon electrochromic operation, particle (grain) size decreases, especially the larger size particles. For two devices made from different nanoparticle size-distributions, we note that particles of 4 nm size undergo no further reduction in size (Table II). These devices exhibit lesser extent of yellowing (but with lower CR). This can be understood in terms of their higher columbic charging energy ($\sim 1/\text{size}$) for smaller particles. Atomic absorption spectroscopy of the electrolyte from yellowed devices revealed significant amounts of Sb, Table II.

We consider yellowing mechanisms consistent with our experimental results. Although we were unable to detect charge-transfer complexes of Sn or Sb within the sensitivities of the analytical techniques employed, it is plausible that low concentrations of spatially isolated (i.e., not reversibly oxidized/reduced by chemical or electrical means) could cause yellowing. The observed decrease in the ATO-electrode particle size and the Atomic absorption detection of Sb/Sn in electrolyte implicates electrode corrosion. Migration and redeposition of electrolyte-borne corrosion products on the electrode surface could also lead to insulating colored films of complex oxides. A plausible example is cathodic formation of amorphous and sparingly-soluble LiSb(V)O_3 ¹⁶ during grounding, through $\text{Li}_4\text{Sb(III)}_2\text{O}_5 + 1/2\text{O}_2 \rightarrow 4\text{e}^- + 2\text{Li}^{+4} + 2\text{LiSbO}_3$ reaction, involving dissolved oxygen from electrolyte or from the SnO_x lattice. Also, if an electrochemical p-doping of the n-type ATO through insertion of Li ions by displacing Sb/Sn ions were to take place then resulting carrier-depleted p-n junctions could form a colored film. Reported synthesis of p-type SnO_x with LiCl by high temperature pyrolytic method¹⁷ supports this possibility. Thus, limiting the extent of Li ion insertion with uniform small-size electrochromic ATO particles (<5 nm) emerges as a new strategy for improving device-longevity.

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Table I. Electrochemical impedance analysis. For data collection 5 mV rms voltage was used. Sample 1 and Sample 2 contained different particle size distributions (see Table II).

Sample description	R_s (Ω)	C (μ F)	R_p (Ω)	W ($\Omega/\text{sec}^{0.5}$)	χ^2
<i>Sample 1</i>					
Fresh	13.5(1)	9(6)	0.5(1)	65(1)	8.7×10^{-5}
Yellowed	16.4(2)	7(2)	1.9(2)	200(4)	2.8×10^{-4}
Yellowed (2 yr.)	300(100)	0.00005(2)	700(100)	20000(2400)	1.3×10^{-2}
<i>Sample 2</i>					
Fresh	24(1)	0.3(2)	8(1)	100(20)	4.9×10^{-3}
Yellowed	27(2)	0.13(6)	12(2)	400(50)	6.6×10^{-3}

Table II. Summary of experimental results for Powder X-Ray Diffraction (SnO_2) and Atomic Absorption measurements for Samples 1 and 2. Common antimony oxides, i.e., Sb_2O_3 (Senamontite), Sb_2O_4 (α -Cervantite, β -Clinocervantite, β -Cervantite), and Sb_2O_5 , exhibit reflections at 27.7° , (25.8° , 27.7° , 27.5°) and 27.3° , respectively; hence the additional peak (at 26.6°) may originate from a distorted Casserite structure.^a

	Condition	Peak position (3σ)		Crystal size ^e (nm)		Etched material ($\mu\text{g}/\text{cm}^2$ Cathode)	
		1	2	1	2	Sn	Sb
Sample 1	Untreated	26.52(1)	26.66(1)	41(4)	8.7(3)		
	Chem. Oxidized ^b	26.54(1)	26.69(1)	38(3)	8.4(3)	12 [4]	50 [8]
	Oxidized ^c (e)	26.56(1)	26.59(1)	24(1)	4.58(5)		
	Reduced ^d (e)	26.55(1)	26.53(1)	27(2)	4.5(3)		
Sample 2	Untreated	26.57(1)	26.66(1)	32(5)	3.9(1)		
	Chem. Oxidized	26.55(1)	26.59(1)	30(4)	4.0(1)	0.8 [0.7]	36 [7]
	Oxidized (e)	26.62(2)	26.63(1)	19(3)	3.9(1)		
	Reduced (e)	26.55(1)	26.62(1)	28(4)	4.1(1)		

^a Numbers in parenthesis give standard deviations for the last quoted digit.

^b Chemical oxidation was accomplished by coating the devices with ordinary household bleach.

^{c,d} Electrochemical (e) oxidation and reduction was carried out by charging the devices in a LiCl bath for a period of 72 h at 1.5 V.

^e The crystal size (t) was evaluated using the Debye-Scherrer equation.

Figure captions

Figure 1. Schematic Diagram illustrating the ‘side-by-side’ design of a printed electrochromic display¹⁸. (Color Printing)

Figure 2. (a) Sn Mössbauer spectra from control (bottom) sample 1 and aged (top) sample 3 electrodes: The peaks are only observed at 0.00 mm/s corresponding to Sn(IV). [Tin isomer shift (IS) values (peak position) of about 2.6 mm/s, 2.6-4.6 mm/s and -0.3-1.9 mm/s for Sn(0), Sn(II) and Sn(IV), respectively]. (b) First derivative Sb XANE spectra from fresh and aged devices, along with spectra from model compounds, Sb₂O₃ and Sb₂O₄ (a mixture of Sb₂O₃ and Sb₂O₅). The fresh and aged samples only shows the presence of Sb(V).

Figure 3. (a) Plots of contrast ratios vs Voltage depicting hysteresis. The “coercive” voltage V_c is approximately 0.2 V (see text). (b) Development of b^* during charging, where the slope of b^* vs $\ln(t)$ is 0.53 ± 0.04 for both curves.

Figure 4. Impedance spectra from ATO EC fresh (left) and yellowed (right) cells. Lines indicate best fit obtained from Zsimp. [The data was fitted to the Randle’s equivalent circuit model (inset) from Zsimp].

Figure 5. NLSFIT of three Gaussians for reflections in the 24-29° (2θ) region from the EC devices. Vertical lines indicate peak positions. The dotted and dashed lines show the deconvoluted peaks arising from large size (dotted) and smaller size (dashed) nanoparticles. The thick shaded curve corresponds to TiO₂ reflection, which provided an internal calibration standard for 2θ scale.

Figure 1.

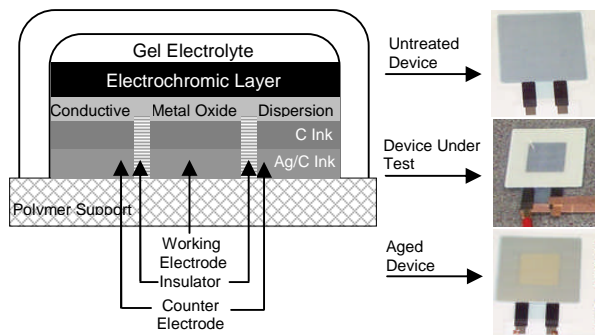
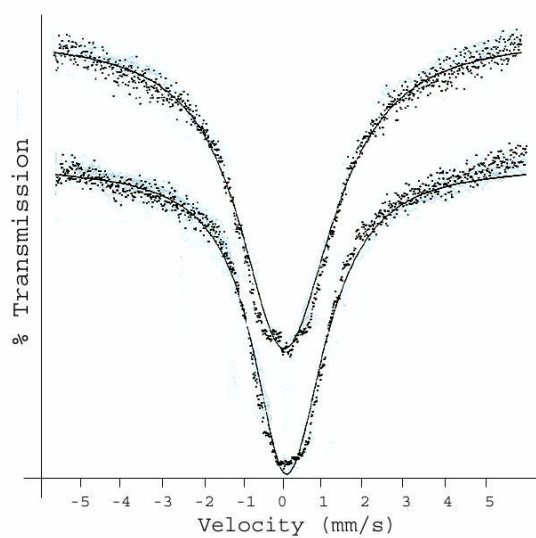


Figure 2.

(a)



(b)

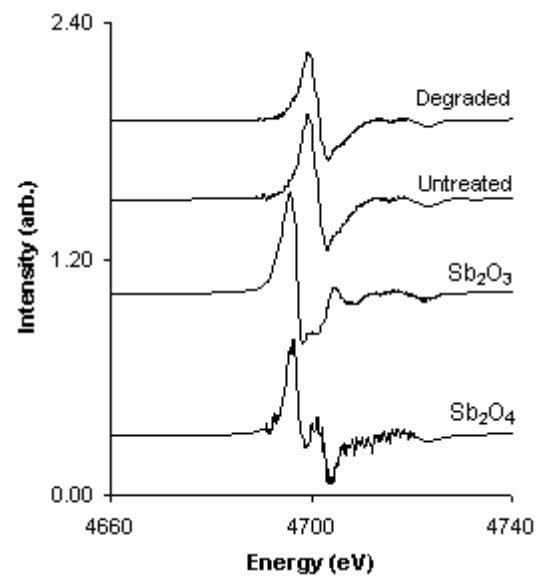
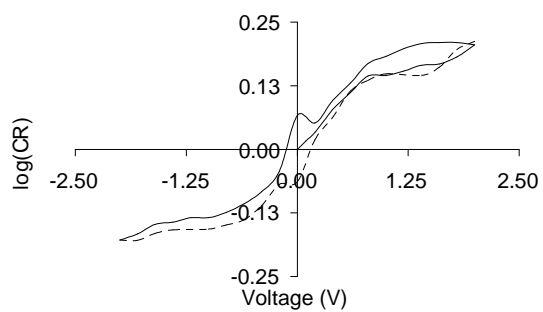


Figure 3.

(a)



(b)

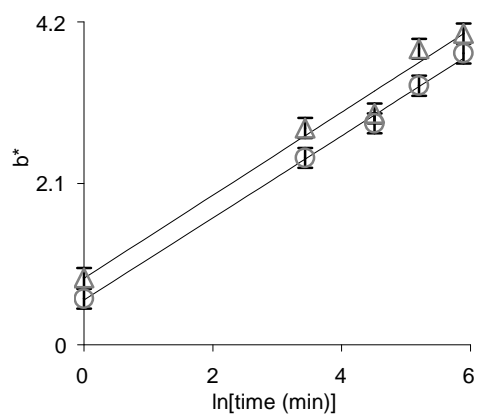


Figure 4.

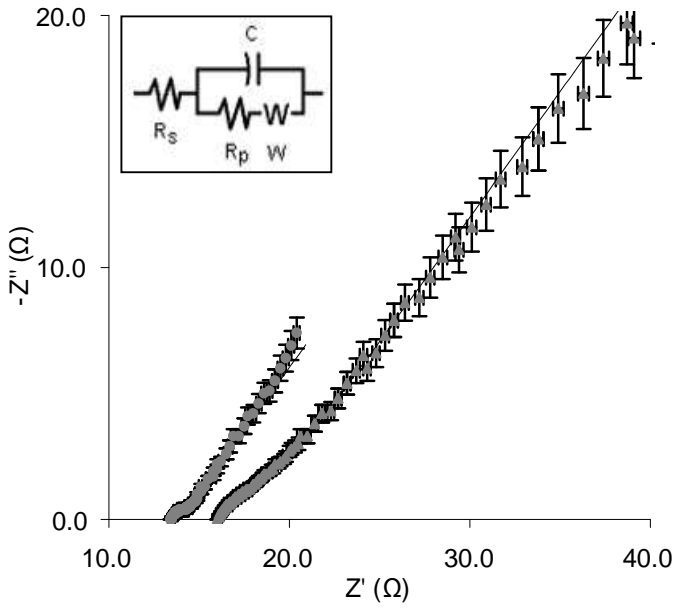


Figure 5.

