

# Unexpected Yellow–Blue Electrochromism of ITO Powders at Modest Potentials in Aqueous Electrolytes

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## Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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Tin-doped indium oxide (ITO) powders, both commercial and laboratory samples, have been incorporated into diffuse-reflecting, interdigitated electrochromic displays using aqueous electrolytes. A surprising yellow–blue electrochromism has been observed which has the features of operation at low potential, minimal charge consumption ( $<10 \text{ mC cm}^{-2}$ ), reasonable switching speed (ca. 1 s) and impressive lifetime ( $>500\,000$  cycles). The observed electrochromic effect is attributed to a combination of changing the effective ITO band gap and populating/depopping the conduction band. Smaller primary ITO crystallites were shown to lead to an enhanced effect, as does increasing tin dopant level to 25 mol%. Increases in dopant level beyond 25% gave no further improvement. Cyclic voltammetry showed no obvious Faradaic process associated with the color changes observed. In addition to obtaining diffuse reflectance spectra, which show that contrast ratio for these displays actually changes direction at about 500 nm, we also measured CIE  $b^*$ -values, which give a quantitative indication of observed blue–yellow shift. These powders appear to be promising candidates for low cost, low information content displays.

Tin-doped indium oxide (ITO) films have been widely used as transparent electrodes for the construction of electrochromic devices and their optical and electrical properties have been reviewed.<sup>1,2</sup> With non-aqueous electrolyte systems, a wide potential range is available in which to carry out a variety of electrochemical transformations. The cathodic range in aqueous solutions is significantly narrower, with a limit of ca.  $-0.7 \text{ V}$  vs. SCE reported.<sup>3</sup> At more negative potentials, irreversible reduction of the electrode material occurs with loss of conductivity: reductive etching in aqueous acid is, in fact, a technique commonly used for patterning ITO films.

In addition to its use as a passive, supporting electrode for electrochromic displays, ITO has been shown to have sufficient charge-storage capability to suggest its utility as a counter electrode, without the addition of other redox materials. A number of workers<sup>4–8</sup> have shown that, in non-aqueous solutions such as propylene carbonate, lithium may be cathodically inserted, quasi-revers-

ibly, into ITO. At charge densities typically used to switch electrochromic displays ( $15 \text{ mC cm}^{-2}$ ), little or no optical change in the visible region was observed in most of these studies although, at higher charge densities ( $50 \text{ mC cm}^{-2}$ ), a brown coloration was observed in one study.<sup>7</sup>

The reported potential at which lithium insertion into ITO takes place in propylene carbonate has also shown some variability. Cogan<sup>4</sup> reported a voltammetric peak potential for lithium insertion of about  $+0.6 \text{ V}$  vs.  $\text{Li/Li}^+$  ( $\text{Li/Li}^+ = -3.2 \text{ V}$  vs. SCE<sup>9</sup>) at  $50 \text{ mV s}^{-1}$ , whilst Steele<sup>7</sup> reported considerably more positive open circuit potentials of  $+2.7$  to  $+3.0 \text{ V}$  vs. the same reference for films which were charged slowly to  $15 \text{ mC cm}^{-2}$ . Brotherston<sup>8</sup> observed some indications of irreversible lithium insertion and solvent/electrolyte degradation under similar conditions. This variability underlines Granquist's contention<sup>6</sup> that lithium insertion into ITO is strongly dependent on the method of manufacture of the ITO and is not an inherent property.

We have previously described the construction of reflective electrochromic displays using opaque electrodes in an interdigitated design.<sup>10</sup> The general approach

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described in this work was to use as the electrode surface a polymer dispersion of a light-colored, composite conductive metal oxide, printed over a metallic conductor, against which electrochromic color changes of various materials could be observed. During the course of these studies we found that, by balancing light dispersion versus absorption in the conductive metal oxide electrode coating, we could observe a very pronounced electrochromic effect in antimony-doped tin oxide (ATO) powders. Like ITO, ATO has been reported<sup>11</sup> to give only a very weak electrochromism in film form. By using a dispersion of a high surface area powder we were able to enhance the appearance of the observed intensity of the electrochromic switching of ATO by allowing increased access of electrolyte to the metal oxide surface and by promoting multiple internal reflections of the light, thus improving the overall efficiency of absorption and the switching speed. An increased level of the dopant antimony, partially responsible for the blue-gray color of ATO, up to about 40%, further improved the observed contrast.

Given the enhancements in electrochromic effects observed with ATO powders, we have initiated a study of other materials in powder form and our preliminary results with ITO are reported here.

## Experimental

*Commercial ITO samples.* Samples of ITO needles and ITO spherical powder were obtained from Sumitomo Metal Mining Co. (Tokyo) and Passtran ITO powder was obtained from Mitsui Mining and Smelting Co. (Tokyo).

*ITO synthesis.* All chemicals were reagent grade (Aldrich) unless otherwise specified. A typical synthesis of ITO powder is as follows.  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (0.85 g, 0.0038 mol) was dissolved in 37% HCl (20 mL).  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  (10.0 g, 0.034 mol) was dissolved in water (20 mL) and added to the tin solution in a beaker. The mixture was heated, with stirring, to 90 °C then neutralised to pH 7 by the dropwise addition of 15% sodium hydroxide solution. When the neutralisation was complete, the heat was turned off and the mixture was allowed to cool, with stirring, for 3 h. The solids were then filtered off, washed with deionised water ( $3 \times 250$  mL) and dried under vacuum at 110 °C for 3 h. A portion of the dried solid was then fired at 600 °C, in an open ceramic crucible, in air, for 3 h.

*Test electrodes.* The test electrodes used in this study were fabricated as described previously.<sup>10</sup> A square working electrode ( $2.54 \times 2.54$  cm) was surrounded by a coplanar counter electrode (1.27 cm wide). The electrodes were screen-printed using (i) silver-carbon ink, (ii) a layer of carbon ink and (iii) a layer of ink prepared from antimony-tin oxide on  $\text{TiO}_2$  (Mitsubishi W-1) in a fluoroelastomer (Viton) binder. The resulting test elec-

trodes were almost white in color and upon these were deposited dispersions of the ITO powders in fluoroelastomer (Viton), dissolved in 2-butoxyethyl acetate, using a drawbar ( $1.2 \times 10^{-3}$  cm). Drying was done at 130 °C for 10 min, and pigment to binder ratio was typically 2.5:1.

*Electrolyte.* The electrolyte used in this study consisted of 25% aqueous lithium chloride solution thickened with 5% polyacrylic acid (Rohm and Haas Acrysol ASE-95). This was applied as a layer about 0.25 mm thick and sealed with a clear, adhesive polyester film.

*Electrochemical measurements.* Cyclic voltammetry was carried out with a PAR model 273A potentiostat using M270 software. Variable applied voltage experiments utilised a PAR 173 potentiostat/galvanostat driven by a Hewlett-Packard 33120A function generator. Electrode potentials were monitored using a calomel electrode and a Hewlett-Packard 54501A digitising oscilloscope. Coulometry was accomplished with a model 640 digital coulometer from the Electrosynthesis Company. Lifetime studies were run with a custom driver operating at  $\pm 1.5$  V (0.3 Hz) from two D-cells.

*Optical measurements.* Integrated reflectance measurements were made with a Nikon Microphot FXL microscope fitted with a Melles-Griot photodiode. A dark-field attachment was used to exclude specular reflectance. The output of the photosensor amplifier was displayed on a Hewlett-Packard 54501A digitising oscilloscope and the system was calibrated using a Kodak black/white standard. Diffuse reflectance spectra and CIE values were obtained with a Hunter Lab Ultrascan spectrometer.

*Analytical methods.* X-Ray diffraction studies were carried out using a Scintag/Seifert PAD V automated powder diffractometer with an ORTEC HyperPure germanium crystal (energy dispersive) detector system.

Electrical resistivity was measured by compressing the powders between two stainless steel pistons ( $0.32 \text{ cm}^2$ ) in a Plexiglass holder with a pressure of 82 740 kPa.

Particle size was measured by laser light scattering using a Coulter LS 130 series particle size analyser equipped with a liquid flow attachment, after brief sonication of the powders to break up loose agglomerates.

## Results and discussion

*Commercial ITO powders.* During our screening of commercially available conductive metal oxide powders we obtained samples of three ITO powders, two from Sumitomo and one from Mitsui, as summarised in Table 1. Each of these powders was incorporated in a fluoroelastomer binder into an interdigitated electrochromic test cell, as described above, and cycled at modest voltages in an aqueous lithium chloride gel

Table 1. Analysis of commercial ITO powders.

Sample	In/Sn (mol %)	Resistivity <sup>a</sup> / Ω cm	Average particle size/ μm	Average crystallite size <sup>b</sup> / Å	Color
1. Sumitomo needles	98/2	0.40	30 ± 20 × 3.3 ± 3 <sup>c</sup>	> 1000	Yellow
2. Sumitomo spheres	95/5	0.74	2.09	330	Blue
3. Mitsui Passtran ITO	91.6/8.4	1.0	5.29	147	Olive green

<sup>a</sup>At 82 740 kPa. <sup>b</sup>Calculated from In<sub>2</sub>O<sub>3</sub> 222 reflection. <sup>c</sup>From microscopy image analysis.

electrolyte. In the case of sample 1 we observed virtually no color change, but samples 2 and 3 both displayed a rapid (ca. 1 s) blue–yellow switching, more pronounced in 3 than in 2.

Figure 1 shows diffuse reflectance spectra for all three samples in the cathodic (blue) and anodic (yellow) states. Clearly, with these powders we are observing a spectral shift, for reasons which will be discussed below, in contrast to our observations with antimony–tin oxide (ATO), where we simply observed modulation of reflectance over a broad region of the visible spectrum. It may be noticed for these three samples that reflectance varies inversely with dopant concentration, whilst switching range increases with dopant concentration.

The contrast ratio for this type of display is somewhat difficult to express meaningfully: Fig. 2 shows a plot of integrated reflectance versus time for sample 3, whilst Fig. 3 shows contrast ratio as a function of wavelength. In Fig. 3 we have expressed the contrast ratio as the ratio of Kubelka–Munk functions in the anodic and cathodic states. A log scale was used for this plot in order to see more clearly the change in direction of contrast ratio, i.e. when it becomes less than 1.0.

The Kubelka–Munk units,<sup>12</sup>  $K/S$ , used in preparing Fig. 3, are defined as  $K/S = (1 - R)^2 / 2R$ , where  $K$  is the linear absorption coefficient,  $S$  is the linear scattering coefficient and  $R$  is the fractional reflectance. By taking this ratio, the expressed contrast ratio represents an

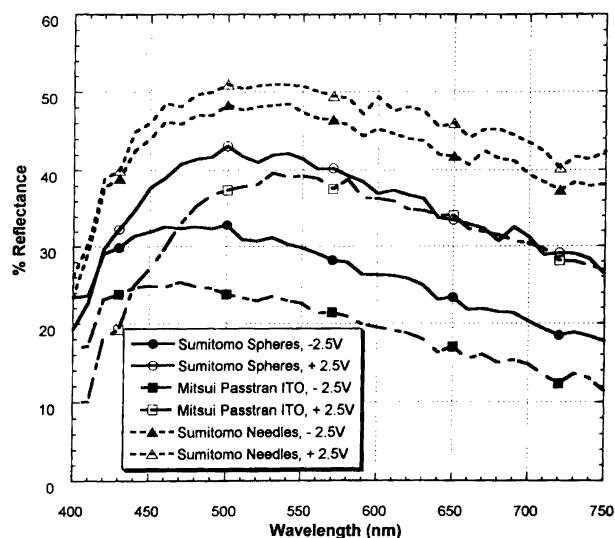


Fig. 1. Commercial ITOs at ±2.5 V applied.

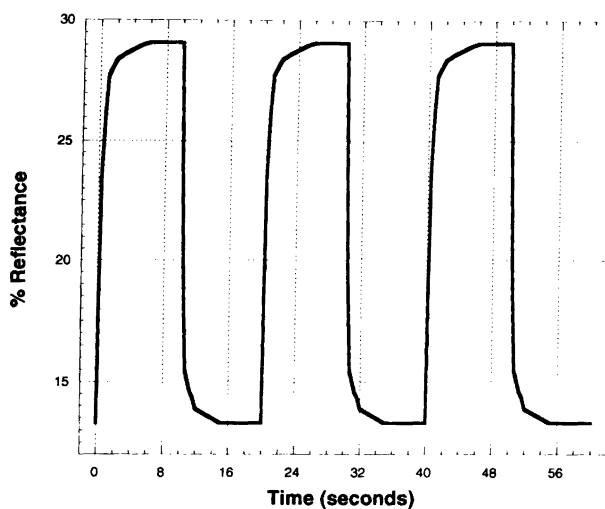


Fig. 2. Reflectance vs. time for Passtran ITO switched at ±2.5 V.

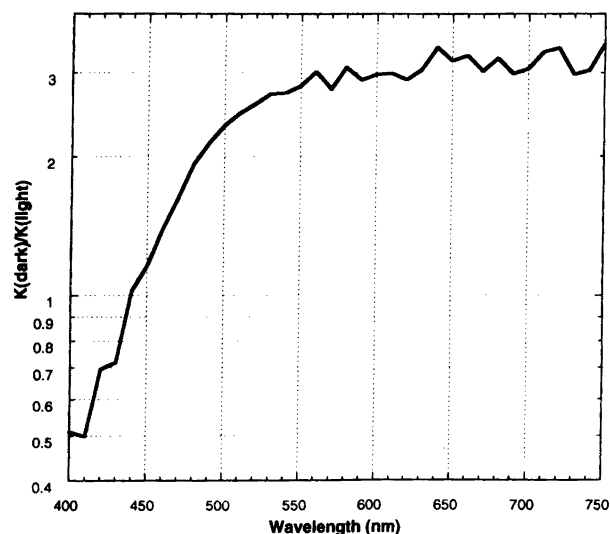


Fig. 3. Contrast ratio vs. wavelength for Mitsui Passtran ITO at ±2.5 V.

optical absorbance-based contrast ratio, as opposed to a contrast ratio of reflectance values more commonly applied to diffusely reflecting systems.

In the integrated measurement in Fig. 2, offsetting effects in different spectral regions tend partially to cancel each other out, detracting from the usefulness of total reflectivity as a measure of contrast. The major value of Fig. 2 is thus to show the timescale on which these

Table 2. Electrochromism of commercial ITO powders.

Sample	$E$ vs. SCE at $\pm 1.5$ V applied	$E$ vs. SCE at $\pm 2.5$ V applied	$\text{mC cm}^{-2}$ at $\pm 1.5$ V applied	Reflection ratio <sup>a</sup> at 700 nm	Blue–yellow shift <sup>a</sup> ( $b_{\text{light}}^* - b_{\text{dark}}^*$ )
1. Sumitomo needles	1.07/–0.53	1.56/–1.09	0.62	1.10	0.93
2. Sumitomo spheres	1.11/–0.81	1.79/–1.13	9.8	1.55	7.47
3. Mitsui Passtran ITO	1.14/–0.92	2.02/–1.06	8.2	2.00	18.53

<sup>a</sup>  $\pm 2.5$  V.

changes take place. Switching times of about 1 s, less at higher applied voltages, are thus attainable.

The displays described above were driven using control of applied voltage. This reflects both the way in which the displays are routinely fabricated (two electrodes/sealed) and our use of voltage driving, as opposed to controlled current, charge or potential, as the basis for producing low cost electronics for commercial operation of such displays. However, in order to understand electrochemical performance better, we clearly need to quantify parameters other than applied voltage.

We have therefore performed measurements of electrode potentials and charge consumption during cycling, as shown in Table 2, as well as cyclic voltammetry shown in Fig. 4. The potential measurements indicate that the blue electrochromism in ITO powder can occur at potentials about 2 V less negative than the voltammetric peak potential for lithium insertion into ITO in propylene carbonate. Charge consumption is quite modest, compared to the commonly quoted standard of  $15 \text{ mC cm}^{-2}$  for electrochromic displays, and optical changes are very significant for ITO, given the small charge involved.

As Table 2 shows, these electrochromic color changes take place over a range of potentials from about  $-1.0$  V vs. SCE at the cathodic (blue) end to  $+2.0$  V at the anodic (yellow) end. However, with variability from sample to sample, electrochromic effects are observed at potentials significantly smaller than these limits. Cyclic voltammetry within this range, as shown in Fig. 4, shows insignificant Faradaic processes, as reported earlier by Kuwana<sup>13</sup> for ITO films in aqueous solutions. The anodic

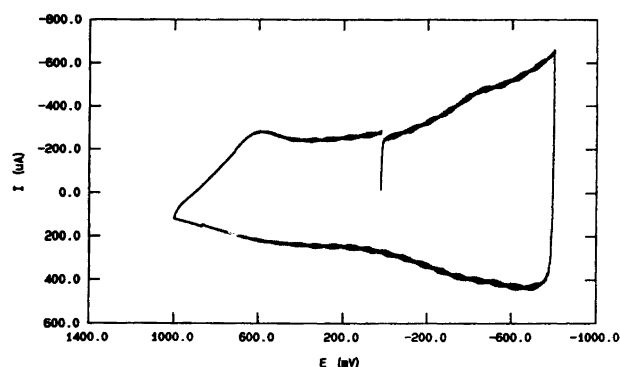


Fig. 4. Cyclic voltammetry of Mitsui Passtran ITO (10% LiCl,  $100 \text{ mV s}^{-1}$ ).

and cathodic limits were reportedly imposed by oxygen evolution and reduction of the metal oxide to a lower valence state, respectively. Between these limits, charge on the film was reported to vary as would be expected for capacitive charging over the potential range of interest to us.

The displays used for this study were quasi-symmetrical, in that both electrodes support the same reaction, albeit in opposite phases. The counter-electrode was larger than the working electrode with the intent that it should not dominate the electrochemistry taking place at the working electrode. As shown below, this has the added benefit that the two electrodes switch in opposite directions at the same time, thus enhancing perceived contrast.

One convenient measure<sup>14</sup> of the yellow–blue electrochromic shift observed in these ITO devices is the CIE 1976  $L^*a^*b^*$  color space system developed for the measurement of reflective color differences.

In Table 2 we also show the difference in measured CIE  $b^*$ -values for the two color states of each powder. This difference is an indication of the magnitude of the observed blue–yellow shift and, clearly, sample 3 shows the biggest shift. Also noteworthy is the significantly lower charge consumption of the coarser-grained sample 1 relative to the other two samples.

By driving these displays too far in the cathodic direction, beyond the capacitive regime and into the Faradaic region, specifically beyond  $-1.3$  V vs. SCE, we have observed rapid, irreversible darkening of the ITO to a brown–black color, caused presumably by the formation of low valence indium and/or tin species. At potentials out to about  $-1.0$  V vs. SCE no damage seems to occur, and sample 3 has been cycled at 1.5 V (applied: see Table 2) for 500 000 cycles (0.3 Hz) with no apparent change in performance.

A few comments on the origin of the observed color changes are in order. As noted above, and shown in Fig. 1, the electrochromic effect with ITO powders consists of an increase in reflectance in the blue visible region upon reduction, with a simultaneous decrease in reflectance at longer wavelengths. Upon oxidation, blue reflectance decreases and longer wavelength reflectance increases. These observations are in agreement with the model described by Granquist.<sup>2</sup> Absorption of shorter wavelength visible light is due to valence band–conduc-

tion band transitions, whilst the broad absorption at longer wavelengths is due to electrons within the conduction band. Upon adding electrons to the conduction band by reduction, the effective band gap increases, the so-called Moss–Burstein effect.<sup>15</sup> The absorption due to the valence band–conduction band transition thus moves down into the ultraviolet region, and blue reflectivity increases. At the same time, red reflectance decreases as the conduction band is populated. The net result is an enhancement of the blue appearance of the ITO. These effects are reversed upon oxidation.

Changes in carrier density of the ITO must necessarily be balanced by cation migration. Whilst we have not studied this phenomenon in detail, it seems likely that, given the speed with which these electrochromic changes occur relative to those observed with solid films, surface effects might dominate the switching behaviour. With the electrolyte used in this work it is possible that either lithium ions, protons or a mixture of both could be responsible for charge balancing. This will be the subject of future studies.

The three commercial ITO powder samples show considerable variation in electrochromic properties, as indicated in Table 2, and these may be understood, at least partially, by reference to the analytical data in Table 1. Electrical conductivity does not seem to be an issue, since all three powders are quite conductive: in fact considerably more conductive than we found was necessary for effective switching of ATO powders in the same type of device.

The major differences between the three samples are in the level of tin dopant, gross particle size and primary crystallite size, as measured by X-ray diffraction. The differences in color reflect differences in oxidation state, or carrier density, of the powders as formed and these in turn are a function of dopant type, firing conditions or annealing conditions after firing.

Chemical treatment of the powders may be used to modify color and resistivity: thus reductive treatment of sample **3** with aqueous dithionite gave a blue-colored powder and slightly lower resistivity (0.18  $\Omega$  cm) whilst treatment with sodium hypochlorite gave a more yellow powder and increased resistivity (395  $\Omega$  cm). Similarly, heating the blue sample **2** in air at 600 °C for 30 min gave a yellow powder with slightly increased resistivity (1.5  $\Omega$  cm). Interestingly, dry milling of sample **3** was also shown to decrease the measured resistivity (0.1  $\Omega$  cm), possibly by removing an oxidised surface layer, although a change in packing of the milled material cannot be ruled out.

A wide range of particle sizes is observed, from large, high aspect ratio needles to small spheres. In general, one would expect the larger particles to give less effective switching, depending on their porosity. High aspect ratio, however, is a plus for electrical connectivity of the particles in a polymer dispersion, the application for which sample **1** was designed. When particle size exceeds

a few microns, we have observed that this leads to a 'grainy' appearance in the display.

It may also be seen from Table 1 and Fig. 1 that electrochromic contrast increases in proportion to dopant level and inversely with crystallite size. It is tempting to speculate that the number of electrons which are labile enough to provide reversible electrochromic switching is determined by the dopant concentration: forcing more electrons into the oxide lattice at higher negative potentials then causes irreversible damage to the host material. The order of electrochromic activity here is thus that predicted from dopant levels.

We have shown<sup>10</sup> a similar correlation between electrochromic activity and crystallite size with ATO: smaller crystallites, and thus many more grain boundaries, would be expected to give greater access of electrolyte to the ITO and thus enhance its activity. However, although there are very significant differences in crystallite sizes, these cannot be decoupled, with these three samples, from the effects of dopant level. Nor can we ascribe differences in crystallite size to differing dopant levels alone, since we do not know the firing conditions used for the three commercial powders.

*Laboratory-made ITO samples.* In order to understand the effects of powder preparation conditions, we synthesised several samples in our laboratory. The synthesis of ITO powder, using tin(II) as the dopant, has been described by Woodhead.<sup>16</sup> A similar sol–gel synthesis of ITO films using tin(IV) was described by Yamamoto:<sup>17</sup> in this case a polymer binder was used for casting the films and could have caused the reduction of tin(IV) to tin(II) on firing.

We prepared a number of samples via precipitation of the hydrated oxides from indium(III) chloride and tin(II) chloride mixtures, followed by firing at 600 °C. These are summarised in Table 3. Our intent was to study the effect of increasing dopant level on electrochromic performance.

The electrochromic performance of the samples in Table 3 was marginally better than that of sample **3**, the Mitsui product, with the sample containing 25% tin dopant giving the best performance. Reflectance spectra for sample **6** at different applied voltages are shown in Fig. 5, along with coulometric and potential measurements.

Within the range studied, dopant concentration exerted only a modest effect on properties. Electrical resistivity increased somewhat with increasing dopant beyond 10%: at the 2% dopant level we suspect that a more significant fraction of the dopant might have been oxidised by firing in air, thus the high resistivity value. Particle size is fairly constant, whilst crystallite size varied only a little. The blue–yellow shift maximised at 25% tin. It is worth noting that for our samples with tin levels higher than 10%, XRD showed the formation of a separate cassiterite phase in addition to the indium oxide. Thus, at these levels the dopant is not contributing optimally.

Table 3. Laboratory-made ITO samples.<sup>a</sup>

Sample	Nominal mol % In/Sn	Measured mol % In/Sn	Resistivity <sup>b</sup> / $\Omega$ cm	Average crystallite size <sup>c</sup> / $\text{\AA}$	Average particle size/ $\mu\text{m}$	Blue–yellow shift $b_{\text{light}}^* - b_{\text{dark}}^*$
4	98/2	98.1/1.9	82.4	141	7.12	24.3
5	90/10	90.9/9.1	2.3	144	5.46	28.9
6	75/25	78.1/21.9	2.7	124 <sup>d</sup>	7.21	30.6
7	50/50	54.3/45.7	11.8	142 <sup>d</sup>	6.75	20.7

<sup>a</sup>Fired at 600 °C. <sup>b</sup>At 82740 kPa. <sup>c</sup>Calculated from  $\text{In}_2\text{O}_3$  222 reflection. <sup>d</sup>Also shows a separate cassiterite phase.

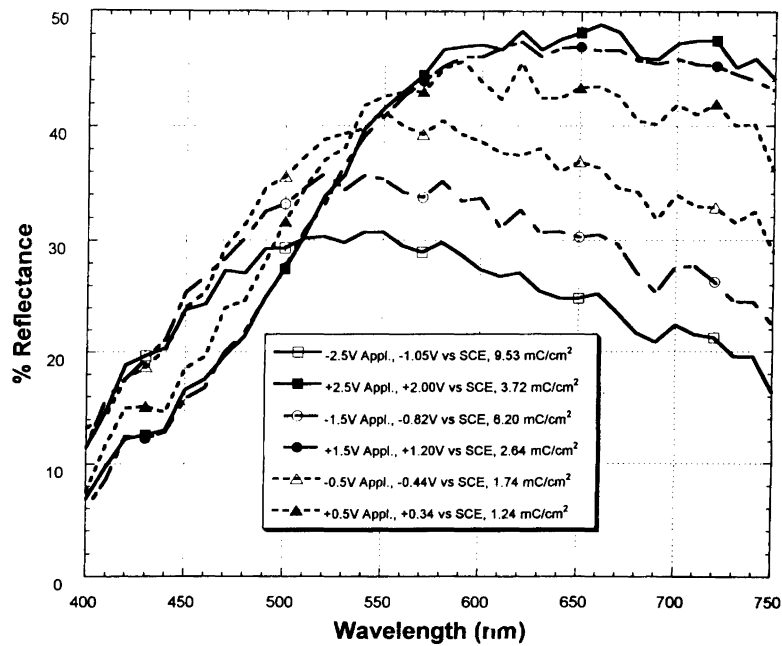


Fig. 5. Reflectance spectra for ITO powder (25% Sn, sample 6).

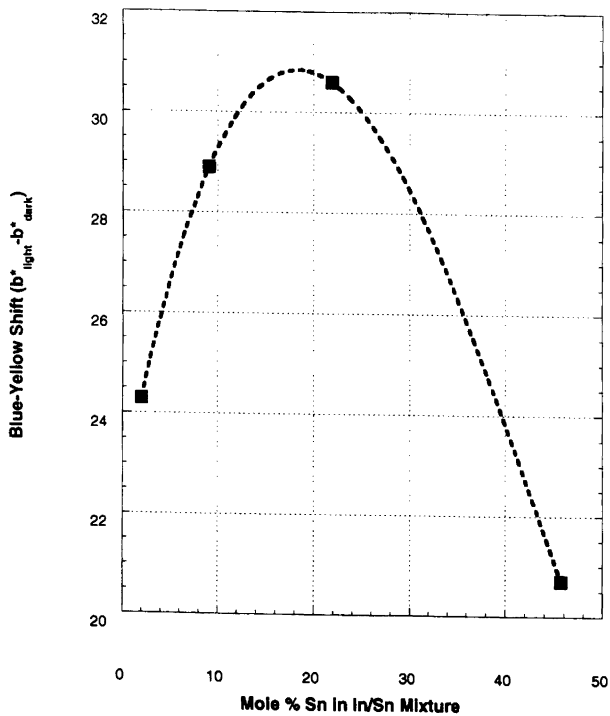


Fig. 6. Blue–yellow shift vs. tin dopant level in ITO powders.

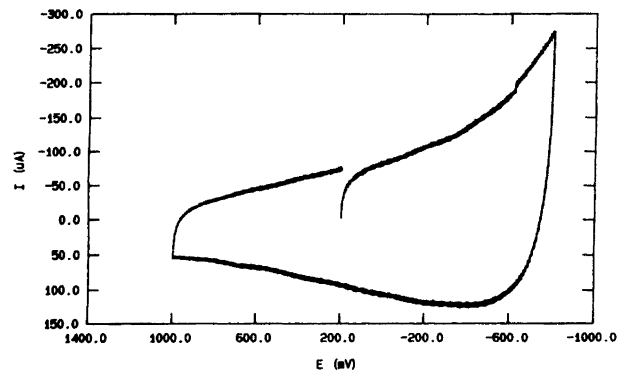
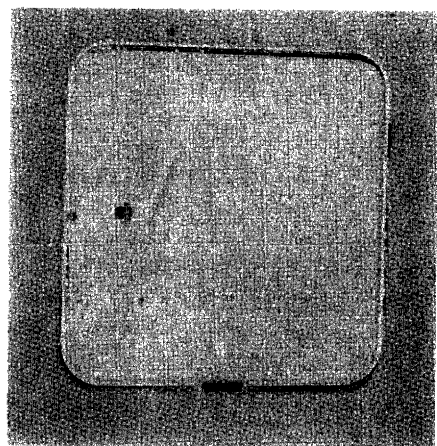


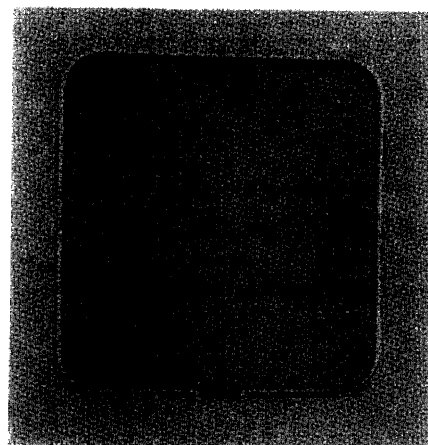
Fig. 7. Cyclic voltammetry of ITO (25% Sn).

Comparing the results in Tables 1 and 3, it appears that the crystallite sizes in samples 1 and 2 are the result of different firing conditions, not an automatic consequence of dopant level. It is apparent from Table 3, by comparing sample 4 to sample 1 in Table 2, that lack of electrochromism in sample 1, the large needles, is primarily due to the coarser nature of the particles and not to dopant level. Sample 4, with the same dopant level but smaller crystallites, gives respectable electrochromism. Figure 6 shows the magnitude of yellow–blue shift plotted against tin dopant level. Clearly there is a trend with

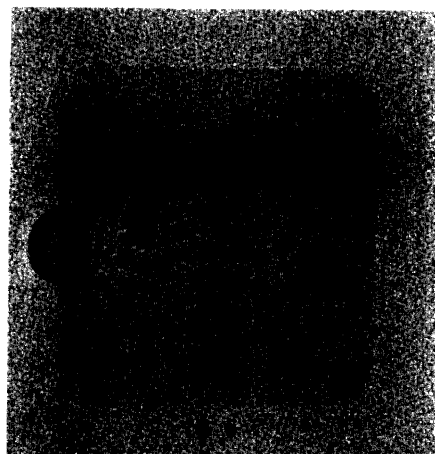


**+ 2.5 v.**

**Sumitomo Needles**

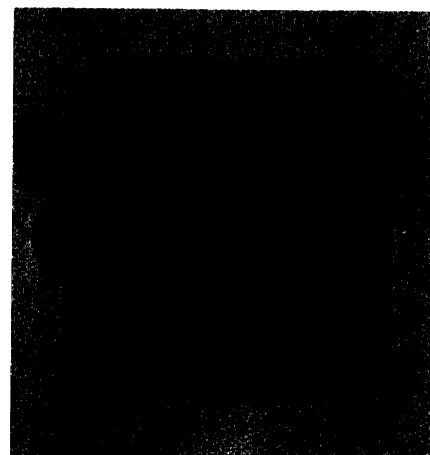


**-2.5 v.**

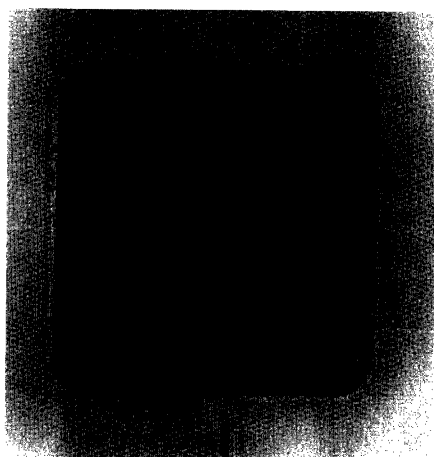


**+2.5 v.**

**Mitsui Passtran ITO**

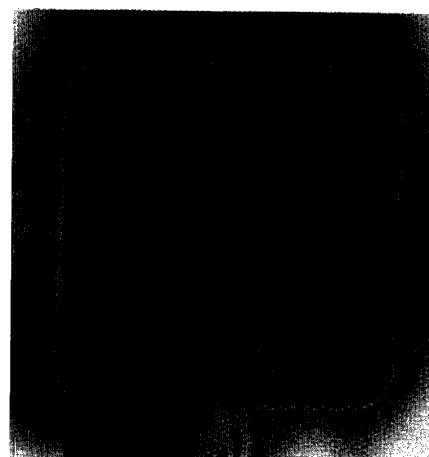


**-2.5 v.**



**+2.5 v.**

**Sample 6 (25% Sn)**



**-2.5 v.**

Fig. 8. Photographic display comparisons.

dopant level but maybe less dramatic than might have been expected.

Charge consumption for these powders is again very low, as shown in Table 4, considering that the composite

films are approximately 10  $\mu\text{m}$  thick, an order of magnitude thicker than most ITO films studied. However, offsetting the greater thickness is the probable lack of participation of a fraction of the powders in the

Table 4. Coulometry of ITO powders.

Sample (%Sn)	mC cm <sup>-2</sup> ( $\pm 1.5$ V applied)	F mol <sup>-1a</sup> (Sn)	F mol <sup>-1a</sup> (Sn+In)	Blue–yellow shift ( $b_{\text{light}}^* - b_{\text{dark}}^*$ )
4 (1.9)	9.3	0.13	0.0026	24.3
5 (9.1)	8.2	0.057	0.005	28.9
6 (21.9)	6.2	0.035	0.008	30.6
7 (45.7)	8.8	0.012	0.006	20.7

<sup>a</sup>Based on weight of coating which varied from sample to sample.

electrochromic process, either because of occlusion by the polymer binder or by lack of electrical connection between particles. Thus, although nominal values are shown in Table 4, we cannot make absolute judgements about the real charge consumption on a mole basis from these experiments.

We briefly studied the effect of firing temperature of these powders in the range 400–800 °C. No major effects were observed in this range: electrical resistivity decreased slightly with increasing temperature and average crystallite size increased somewhat, without impacting electrochromic performance significantly.

In our previous studies with antimony–tin oxide,<sup>10</sup> we routinely observed average crystallite sizes in the 40 Å range, leading us to believe that there is still room for considerable improvement in the performance of ITO powders, should we be able to further decrease crystallite size and homogeneously incorporate more dopant.

The cyclic voltammetry of the 25%-doped ITO powder is shown in Fig. 7 and strongly resembles that of sample 3.

Finally, Fig. 8 shows a photographic comparison of three different materials in the oxidised and reduced states: sample 1, Sumitomo needles, sample 3, Mitsui Passtran ITO; and sample 6, our laboratory sample of ITO with 25% tin dopant.

## Conclusions

We have demonstrated in this preliminary study that ITO powders are potentially useful electrochromic materials in their own right. By using powders composed of relatively small crystallites, and dispersing them in a polymer binder onto an electrode in a reflective display, we have observed significantly enhanced electrochromism compared to similar materials in film form.

By utilising powders, both diffuse optical and transport properties are improved and an attractive yellow–blue electrochromism is observed at potentials attainable in an aqueous electrolyte.

Considerable variation was shown by three commercial ITO powders: a large crystalline powder optimised for conductivity showed a lack of electrochromism more typical of films, whilst two finer powders showed enhanced switching.

Electrochemical studies did not identify a well defined

Faradaic process associated with this electrochromism and, in fact, it appears to be more capacitive in nature. Switching speed is quite good (of the order of 1 s), and charge consumption is modest ( $< 10$  mC cm<sup>-2</sup>) for these displays as presently constituted.

Interesting changes in diffuse reflectance spectra are observed upon switching, yielding a contrast ratio which is a function of wavelength. The contrast ratio actually changes direction at about 500 nm, as a consequence of the electronic changes occurring, in accordance with a previously described model.<sup>2</sup>

Samples produced in the laboratory demonstrated that yellow–blue electrochromic shift may be improved by increasing the level of tin(II) dopant to 25% but further increases in dopant were not effective.

Switching speed, contrast, lifetime and ease of fabrication offer considerable encouragement for the incorporation of ITO powders into low cost, mass-produced electrochromic displays<sup>18,19</sup> for low information content applications. Although we have demonstrated an interesting effect in these preliminary studies, there is no reason to think that further improvements are not possible through synthesis modification and improved display construction.

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