Supplementary Information

for

FTO Darkening Rate as a Qualitative, High-throughput Mapping Method for Screening Li-Ionic Conduction in Thin Solid Electrolytes

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1. FTO darkening system.

FTO darkening is measured, using a home-built system to capture on video the electrochemical process with a maximum time resolution of 0.3 sec (Figure S1). The system consists of three main parts: a white light source (LED), an electrochemical cell and a video camera. The sample holder can accommodate a 7x7cm piece of FTO (covered with the sample that is tested, the cathode); it is separated by 1 cm from a similar holder for the counter electrode (anode), which is a similar piece of FTO. Optionally there is a small aperture between the two electrodes for a quasi-reference electrode.

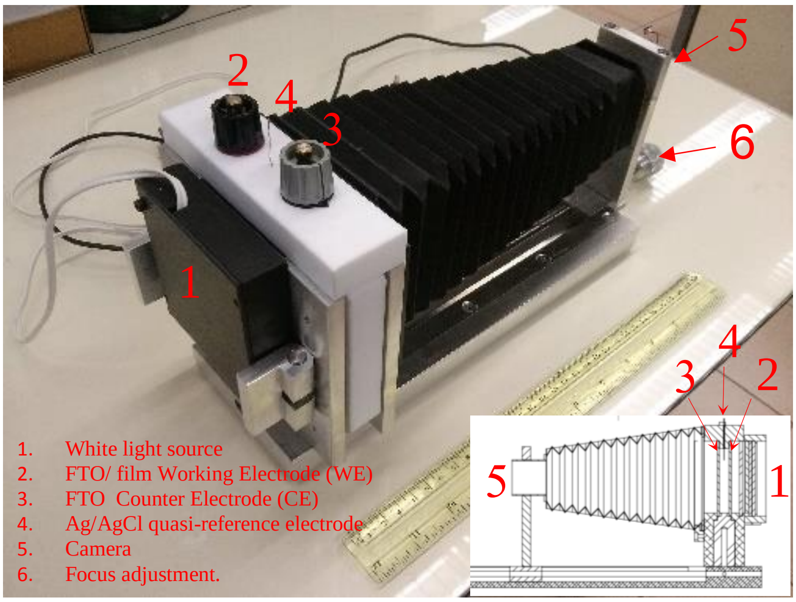

Figure S1. Home-built system to measure FTO darkening. *Insert* show the cross-section of the system. The numbers are explained in the legend.

The two electrodes are clamped to a Teflon frame. A Teflon cover is used to form a sealed cell. Rotating knobs 2 and 3 make electronic contacts to the counter (CE) and working electrode (WE).

The liquid electrolyte that is placed in-between the electrodes closes the circuit. Material compatibility of all parts of the system, including O-rings, pipes and syringes (used to deliver the electrolyte to the cell) with the solvent and chemicals used to form the electrolyte, was checked separately.

A typical darkening experiment started by cleaning the cell with EtOH and DMC. The counter FTO glass was cleaned using saturated $K_2Cr_4O_7$ in 98% H_2SO_4 solution, thoroughly washed with de-ionized water, rinsed with 70% EtOH and dried with compressed dry air.

The two FTO glasses (the one, coated with the thin film that is being tested, and the counter electrode) were clamped to the Teflon frame and ~ 35 ml liquid electrolyte (DMC with 0.4 M $LiClO_4$ and 5 mM Fc/Fc^+) is injected into the cell, using plastic syringe. This volume assures that most of the FTO surface is covered with electrolyte leaving a few millimeters of non-covered film, used to correct for intensity fluctuations and to assure that the liquid electrolyte does not touch the electrical contacts at the upper part of the cell. Care was taken to avoid scratching the film during electrolyte filling to avoid direct electrolyte contact with the FTO substrate of the WE.

The CE and WE and, whenever used, the quasi-reference electrode, were connected to a potentiostat, AUTOLAB, and a potential of 9 V was applied to the CE.

The white light source is an LED panel. The light intensity is tuned by changing the voltage. Care was taken to avoid camera saturation. The light source is turned ON for at least 30 min prior to the darkening experiment. Video capturing was done using a camera that had been focused in advance. The camera is coupled to control software – iSpy, set to capture one frame per second with a resolution of 640x480 pixels and stored in MP4 file format that was later converted to AVI format, compatible with the imaging analyses software used. Such resolution was sufficient to distinguish objects that were separated by 0.8 mm.

2. Video image analysis:

Image analysis was done using ImageJ software. Darkening in bits units is related to a grayscale range from 0 to 255bits. This darkening was obtained from the analysis of captured images using ImageJ software. The linear dependence of darkening rate on optical density (O.D) shown in figure S2, is caused by the formation of Sn particles during darkening process. The higher is the Sn concentration, the more intensive is the color according to the Beer-Lambert law. Since appearance of Sn particles is the result of reduction of FTO, the grayscale in bit/sec reflects the rate of lithium ion migration through the ceramic layer. The O.D is equivalent to absorption, therefore it is presented in logarithmic scale. Bit/sec reflects the rate of the change of the optical density.

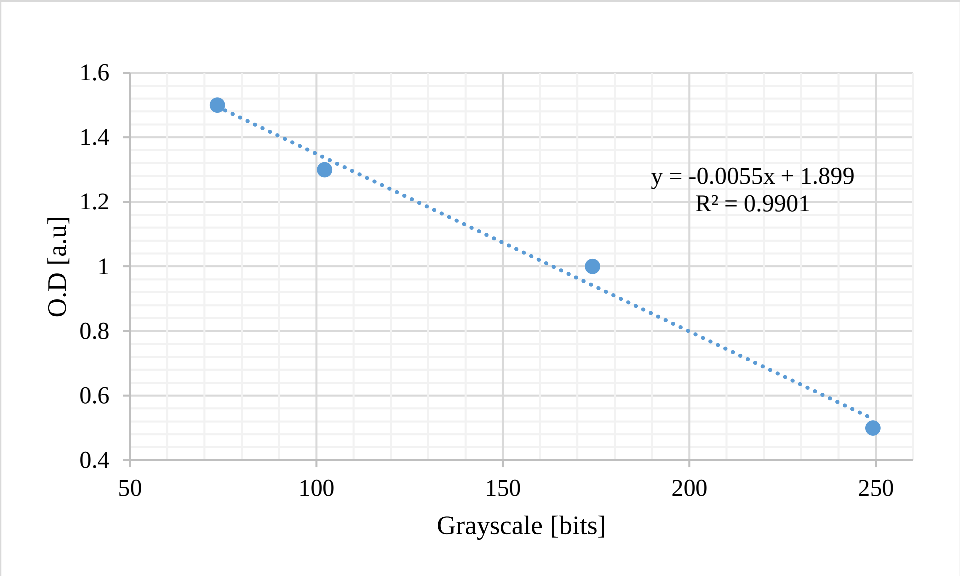

Figure S2. Optical density *vs*. Grayscale test with O.D filters, for calibrating the experimental darkening measurements using the system presented in figure 1S.

The average dark color in video images of a darkening experiment was determined in specific circular regions of 0.026 cm^2, which contain a few tens of pixels, each with a different dark level. Many circular regions were defined in advance using Regions of Interest (ROI) file. Five regions were defined in areas on the film without electrolyte to correct for light fluctuations. In case, the film had back contacts (for Impedance measurements), the ROI were defined in four nearest neighbors to these contacts to get an average value of the darkening rate for comparison with resistance values obtained from impedance measurements.

The darkening rate was obtained by calculating the change in the average dark color with time on each ROI at the onset of darkening. It is actually the slope, at the onset of the darkening *vs*. time plot. Figure S3 shows an example of average darkening in single ROI vs. time. The dark color formed in a few seconds (depending on Li-ion conductivity in the specific ROI) after ON, start of allying the voltage (of the potentiostat). Specifically, in Figure S3, the potential was turned ON 6 sec after starting to capture the video of the darkening process. In this figure, the red and blue lines are guides to the eye only. The blue line illustrates the slope that represents the darkening rate at the onset.

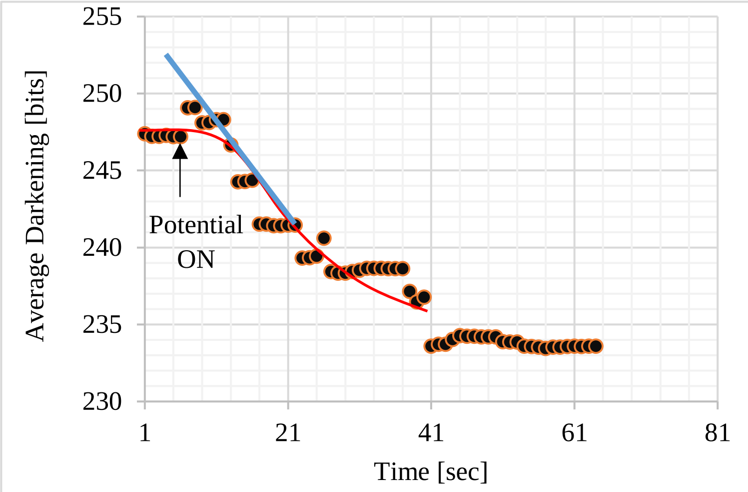

Figure S3. Typical average darkening *vs*. time of single ROI. Darkening rate is calculated from the slope blue line illustration. Red and blue lines are guides to the eye only.

The slope was determined several times. The darkening rate was determined from the average of slopes value and considered as the average darkening rate. This average darkening rate was used in the main text as the darkening rate in bit/sec units. The error in the darkening rate is the deviation from the average value. The darkening rate of bare FTO was evaluated in each ROI to provide a baseline. The average darkening rate of bare FTO under our experimental conditions was -0.43±0.08 bits/sec. Comparing the darkening rate in each ROI, obtained for the sample of FTO coated by ion-conducting film *vs*. bare FTO, helps excluding regions with any film discontinuity that provides direct electrolyte-FTO contact.

Other regions on the film that were excluded are regions that showed blue color spots, which result from Fc^+ accumulation. For example, Figures S4a and S4b are frames taken from a video provided in section 3 of the Supplementary Information. It is possible to see (circled in red) that at about 5 min after starting the darkening process, a blueish color has been formed at the bottom of the frame b. Saturated images in inserts clarifies those reigns even further. We suggest that the blue spots detected at the cathode surface are presumably caused by the formation of insoluble reduction products of Fc^+ thus, indicating the presence of electronically/mixed conducting sites in the deposited film. Note that there is no color change at the counter-electrode (bare FTO), during the entire darkening process.

3. FTO darkening reversibility of library containing Li-La-P-O on FTO.

The attached video (FTO darkening_9V Li-La-P-O) shows a darkening of a film that resulted from depositing Li, La and PO_4 precursors on FTO using spray pyrolysis and subsequent annealing (details are given in the experimental section). Dark dots represent contacts. Note that there are more contacts than in typical tests. An extra set of Au contacts was deposited next to Ag contacts to test the effect of the contact type on impedance measurements. This video captures the darkening process and the reversible brightening.

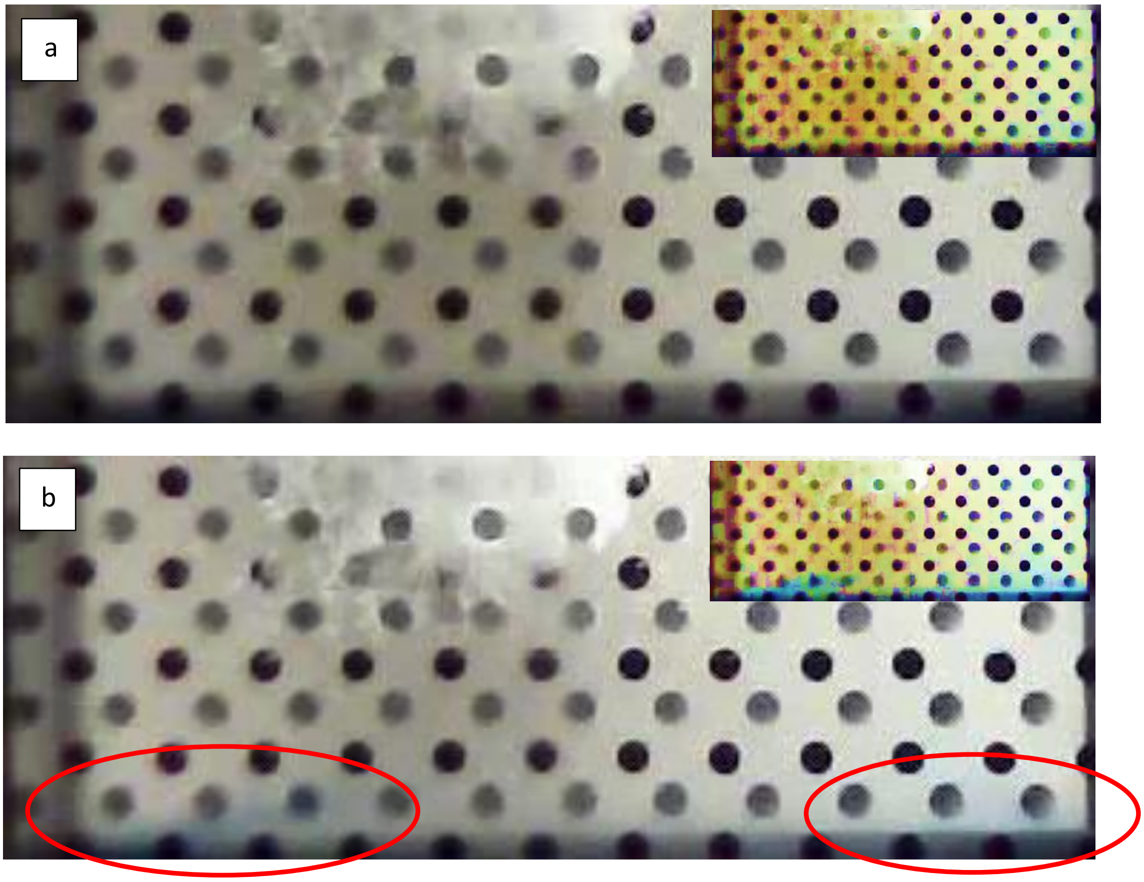

Figure S4. Blue color formation due to accumulation of low-solubility Fc^+ reduction products at sites that are electronically conductive, during FTO darkening. Pictures a and b were taken ~2 min and ~5 min, after darkening started, *i.e.*, after the system was put in its ON state, respectively. Insert are the corresponding images in saturation level of 400%.

4. FTO darkening in all solid-state FTO/Li-La-S-O/Ti system

Two films of Li-La-S-O and La-S-O were prepared on FTO (TEC 15) using a multi-head spray pyrolysis system following the procedure described in the fabrication of Li-ion conducting films. Specifically, since the La-S-O library has been sprayed without LiAc in water, the available spray nozzle was fed instead with water to compensate and to obtain Li-La-S-O and La-S-O films with similar deposition profile. After film preparation, 100 nm Ti contacts were evaporated on the prepared films using a mask to form a circular contact area of 0.026 cm^2. Contact preparation is described in the section on formation of electrical contacts. Note that in this experiment Ti replaces the bare FTO (counter electrode in the liquid electrolyte configuration) as second contact.

Measuring FTO darkening was done using an optical microscope (Olympus AX70) in a reflection mode that was coupled to a photodiode. Figure S5 illustrates the setup, with a (7 cm x 7 cm) glass- FTO/ Li-La-S-O /Ti or FTO/La-S-O /Ti sample in the microscope with the glass side facing the (4x) objective lens.

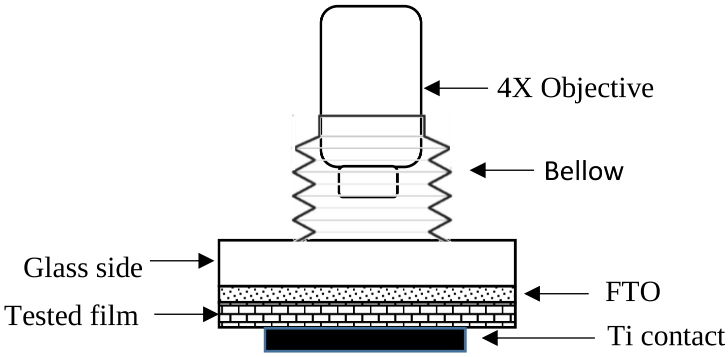

Figure S5. Schematic illustration of the thin Li-La-S-O or La-S-O film sandwiched between FTO and Ti electrical contacts, under the objective lens of the (reflection) microscope.

Darkening in normalized photocurrent intensity (NPI) units is obtained by measuring the current through a photodiode placed after a tested film and a light sources (see SI section 5, 6). The purpose of such a measurement is to get an indication of darkening only. There are no attempts to converts units from NPI to Bits or Visa-Versa. Indeed we expect no linear correlation between NPI or NPI/sec and dark colorant (Sn particles) formation/ formation rate. Therefore there were no attempts to correlates darkening rates in NPI/sec with any of the physical properties of tested films.

The photocurrent generated by the photodiode was measured with a pico-ampermeter (Keithley 6485), coupled to a potentiostat (AutoLab PGSTATE20) for photocurrent logging. Photocurrent sampling was done each 0.5 sec. Care was taken to exclude any ambient light during measurements. Light contamination was tested with external light to confirm that the photodiode signal did not change with intensity of external light source. Voltage was applied with a Keithley source meter 2410 with positive and negative poles connected to the Ti (contact) and FTO (cathode), respectively.

Darkening tests were performed at ambient room temperature. Prior to measurements, we performed conductivity tests to confirm that the sample was not shorted due to probe punching. The thickness of Li-La-S-O and La-S-O films were 4.25 ± 0.25 μm, 5.25 ± 0.25 μm, respectively. Film thickness and electrical resistance were measured using a (DektakXT Bruker Stylus) profilometer and a Keithley source meter 2410, respectively.

Photocurrent measurements started without applied potential, *i.e.*, in the OFF condition. Typically, darkening tests started at a low ON potential, which was increased until darkening could be measured. The timing and magnitude of the ON and OFF potentials that were used in each case are given in the results.

The photocurrents were averaged over 30 sec of measurements. The ratio of the average photocurrent to the initial photocurrent (Normalization) is presented in the results with typical relative error of 0.007% that was calculated from the standard deviations of the averaged photocurrent during the potential OFF time.

5. FTO darkening tests in a wet electrochemical cell.

FTO darkening tests were conducted using a wet electrochemical cell made from Teflon, customized for a small sample (2x5x0.3 cm^3). The cell was put in-between a photodiode and LED at opposite sides of the cell. This cell served a few experiments with different experimental parameters to meet different needs. For example, when Ti metal was tested as a non-Li conducting material, it also blocked almost all light. Therefore, the LED was run at its maximum to get enough light through the sample to the photodiode, which for this experiment, was replaced with a larger area one. Table S1 summarizes the parameters used in each experiment. Each experiment is labeled as follows: 1. Electrolyte with and without Li. 2. Non-Lithium conductor, 3. FTO darkening reversibility.

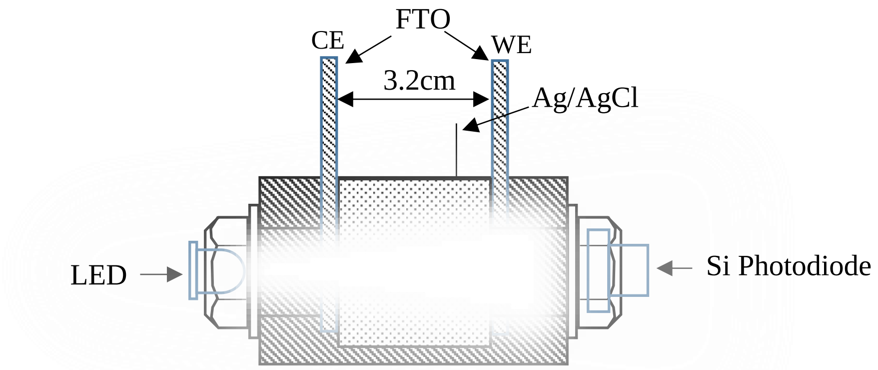

Figure S6. Schematic view of the electrochemical cell used to run the control experiments.

Table S1 summarizes the parameters used in each experiment for running the electrochemical cell, described above.

Exp.	Sample	Electrolytes	LED[a]		Cell potential	Si-Photodiode
			V [V]	I [mA]		Detection area [cm^2]
1	Bare FTO	7.2μS/cm $LiClO_4$ in DMC 7.2μS/cm $NaClO_4$ in DMC	10	18.45	9 V [b]	0.33 [c]
2	Ti on FTO Ti on Glass	7.2μS/cm $LiClO_4$ in DMC	12	23.69	21 V [2]	0.95 [d]
3	Bare FTO	0.4M $LiClO_4$ in DMC	10	18.45	-3.5V *vs* Ag/AgCl [e]	0.33 [c]

[a] Potential applied using Keithley SourceMeter 2410.

[b] Potential applied using Keithley SourceMeter 2450.

[c] Photocurent generated from photodiode was measured using potentiostat (μAutoLab) in chrono-amperometric mode.

[d] Photocurent generated from photodiode was measured using a potentiostat (AutoLab PGSTATE20 in chrono-amperometric mode).

[e] Potential applied using potentiostat (AutoLab PGSTATE20 in chrono-amperometric mode).

Prior to all experiments, the LED light was turned on ~ 30 min before starting an experiment. Care was taken to avoid ambient light contamination. In experiment c, the potential was turned ON (for a few seconds) and then OFF (for tens of seconds) a few times, when FTO darkening reversibility was tested. The timing of this switching on and off of the light source is reported in the main paper.