Supporting Information:

Defect quantification in metal halide perovskites: The solid-state electrochemical alternative

Michel De Keersmaecker, *** Neal R. Armstrong, and Erin L. Ratcliff *** ***

†Department of Chemical and Environmental Engineering, Laboratory for Interface Scienceof Printable Electronic Materials, The University of Arizona, 1133 E. James E Rogers Way, Tucson, AZ, 85721, USA

‡Department of Chemistry and Biochemistry, The University of Arizona, 1306 E.University Way, Tucson, AZ, 85721, USA

¶Department of Materials Science and Engineering, The University of Arizona, 1235 E.James E Rogers Way, Tucson, AZ, 85721, USA

E-mail: mdekeersmaecker@email.arizona.edu; ratcliff@email.arizona.edu

Phone: +1 520 6265567

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S1 Experimental procedures

S1.1 Materials

Precursor solution solvents. N, N-dimethylformamide (DMF, anhydrous, 99.9%, Sigma Aldrich), dimethylsulfoxide (DMSO, 99+%, Alfa Aesar) and chlorobenzene (extra dry, 99.8%, Acros Organics). These precursor solution solvents were extensively dried over freshly activated molecular sieves before use and degassed for 30 minutes with argon before transferringto nitrogen glovebox (< 1 ppm O₂, < 0.1 ppm H₂O). The molecular sieves were activated ina muffle oven for 3 hours at 320 °C.

Precursors. Lead iodide (PbI₂, 99% trace metals basis, Acros), methylamine (MA, 40% in H₂O, Sigma Aldrich), and hydroiodic acid (HI, 47+%/stabilized, ACS grade, Sigma Aldrich). All precursor materials were kept in a desiccator under vacuum to avoid water contamination.

Electrolyte. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Sigma Aldrich), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI], 99%, IOLITEC), and acetone (ACS, 99.5%, Beantown Chemical). The ionic liquid was kept in a N₂ glovebox.

S1.2 Preparation of the MAI precursor

Methylammonium iodide (MAI) was prepared by adding ca. 25 mL of ice bath-cooled MA into ca. 100 mL of ethanol in a 250 mL round bottom flask (RBF) in air at room temperature. HI, cooled in an ice bath, was slowly added (ca. 10 mL) to the RBF. The solution was stirred for ca. 24 hours in air at RT. Before rotary evaporation, the solution was dried with anhydrous magnesium sulfate and vacuum filtered in air to remove the magnesium sulfate-water complex. The MAI solution was then rotary evaporated lending a white precipitate. MAI was re-crystallized/purified by 1) re-dissolving orange precipitate in a minimal amount of ethanol, 2) supersaturating the solution with an applied heat gun to the RBF, 3) slowly cooling the RBF in an ice bath. The collected solid was

then filtered in air and rinsed with ice bath-cooled ether that had been dried under activated molecular sieves for 1 hour in air. This recrystallization process was performed twice to collect white crystals. The collected crystals were then vacuum dried at 90 °C overnight before transferring to a desiccator under vacuum for storage until use in perovskite thin film deposition. All perovskite precursors are kept in a desiccator under vacuum to avoid water contamination.

S1.3 Preparation of the perovskite active layer

ITO coated glass slides (sheet resistance 9 - 15 $\Omega \Box^{-1}$, Colorado Concept Coatings LLC, 96041) were cut to individual samples (10 x 10 x 1.09 mm³). All ITO substrates were pre-rinsed and sonicated in solutions of sodium dodecyl sulfate-water, acetone (ACS, 99.5%, Beantown Chemical), and finally isopropanol (ACS, 99.5%, Beantown Chemical), and allowed to dry.

S1.3.1 Preparation of PbI2-rich or over-stoichiometric MAPbI3 films

To deposit PbI₂-rich MAPbI₃ films, ca. 461 mg PbI₂, and ca. 159 mg of MAI are weighed in air. Both salts were transferred in two separate hot 2-dram vial (stored at 150 °C in an oven to minimize water content) and then loaded into a N₂ glovebox. In the box, 950 μ L of DMF and 105 μ L of DMSO were added to both vials and then mixed in a third vial. This precursor solution was then stirred at 70 °C for 15 minutes. Subsequently, the solution was cooled down for 5 minutes and filtered with a 0.25 μ m PTFE syringe filter to obtain the precursor solution. The precursor solution was dispensed onto the cleaned ITO substrates (120 μ L) at room temperature and then spin-cast at 6000 RPM for 30 seconds (6000 acceleration). After 20 seconds of spinning, 300 μ L of chlorobenzene (anti-solvent) was added. The film was left in the spin coater for 1 minute and then transferred to a preheated hot plate 100 °C to anneal for 60 minutes.

S1.3.2 Preparation of PbI₂-poor or near-stoichiometric MAPbI₃ films

MAPbI₃ films were deposited by weighing ca. 324 mg PbI_2 , and ca. 102 mg of MAI in air.Both salts were transferred to a hot 2-dram vial (stored at 150 °C in an oven to minimize water content) with a micro stir bar and then immediately loaded into a N₂ glovebox. Within the N₂ glovebox, 512 μ L of DMF and 128 μ L of DMSO were added to the vial (generating solution concentrations of ca. 1:1 M for MAI:PbI₂, respectively) and then the precursor solution was stirred at 70 °C for 20 minutes. The yellow solution was then allowed to cool down to room temperature and then filtered with a 0.25 µm PTFE syringe filter. The precursor solution was dispensed onto the cleaned ITO substrates (30 μ L) at room temperature and then spin-cast at 1000 RPM for 10 seconds (6000 acceleration) followed immediately by 6000 RPM for 20 seconds (6000 acceleration). With five seconds remaining on the spin-coating cycle, 100 μ L of chlorobenzene (anti-solvent) was added to the film in a clean dispensing motion as close to the center of the spinning film as possible. All MAPbI₃ films were incubated for 1 minute at room temperature in a plastic petri dish with a plastic lid before being transferred to a hot plate for 60 minutes at 100 °C as the final thermal annealing step inside the N2 glovebox. This 1-minute incubation time, followed by the annealing step, ensures conversion to the perovskite product, avoiding excess PbI2 formation. Glovebox atmosphere circulation (i.e., over an internal purifying catalyst) was kept off throughout the film processing steps described above. After each day of experiments, the glovebox atmosphere was purged for ca. 20 minutes before turning back on the purifier circulation (i.e., until the next experiments involving film processing). MAPbI₃ films are kept in the N₂ glovebox until they are used for surface and electrochemical characterization.

S1.4 Three-electrode device construction

S1.4.1 Preparation of IL-based solid electrolyte with and without redox probe

The electrolyte was made by adding 1 g poly(vinylidene fluoride-co-hexafluoropropylene) or PVDF-HFP pellets to 10 g acetone. The solution was stirred overnight in air on a hot plate set at 50 °C. When dissolved, 1 mg of the redox probe (ferrocene) is added to the cooled solution. To make a 16 wt% IL containing electrolyte solution, 160 mg 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide or [EMIM][TFSI] (stored in a glovebox) was dissolved in 1 g of the PVDF-HFP/acetone solution. The entire solution was then emptied in a rectangular watch glass (35 x 40 mm²) and was allowed to dry in air overnight. This solid-type electrolyte with this exact composition has been shown to be a non-solvent for most lead halide perovskite films.

S1.4.2 Preparation of perovskite device structures

First, a silver foil (5 x 13 mm², 99.9% metals basis, Alfa Aesar) was polished with 4000 grit sandpaper and sonicated in deionized water. Using a two-electrode cell filled with 1 M HCl (ACS, 36-38%, EMD) and a Pt counter electrode, we chlorodized the silver foil at 0.4 V for 2 minutes. Three-electrode sandwich-type perovskite device structures were constructed as a 5-layered stack consisting of an ITO film transparent electrode on glass, a MAPbI₃ film as the active layer, a solid electrolyte film (with or without redox probe) wrapped around an Ag/AgCl foil and a gold electrode. The gold electrode was cleaned and sonicated in ethanol (anhydrous, >95%, Decon Laboratories Inc.) before use. The device stack was pressed and kept together using two thin metal plates tightened with four screws. All device structures were assembled and tested in ambient atmosphere.

S1.5 Perovskite film characterization

S1.5.1 θ/2θ X-Ray Diffraction (XRD)

For $\theta/2\theta$ -XRD experiments, MAPbI₃ films on ITO were mounted on a clay holder in air and loaded into a Phillips X'PERT MPD system, with "PreFIX" source module and a "X'Celerator" detector module, using CuK_a radiation ($\lambda_{max} = 1.541874$ Å) with electron gun cathode-anode power settings of 45 kV at 40 mA). Films were analyzed from 5° to 90° in 2 θ with 0.0167° step size, scanning symmetrically (i.e., source and detector at same angle with respect to the surface normal – thus preferentially detecting scattering from crystal planes parallel to the substrate plane) with a total scan time of approximately 35 minutes. Optical hardware settings include a 0.04 rad soller slit (source and detector side), a 2° divergence slit at 140 mm from sample (source side), a 11.6 mm horizontal mask (source side), a 0.02 mm-thick Nickel filter (source side), and an overhead sample beam knife. Processing/Analysis of XRD patterns were performed with X'Pert HighScore (for background subtraction) and Mercury 2020.3.0 software (for identifying Bragg peaks from crystal structure).

S1.5.2 Photoelectron spectroscopy

XPS (monochromatic Al_{Ka} excitation at 1486.3 eV, 10 mA, 15 kV, pass energy of 20 eV) spectra are acquired at a photoelectron take-off angle of 0°, 30° and 60° (normal to the surface) using a Kratos Axis Ultra PES system (Kratos Analytical, USA) in ultra-high vacuum with a base pressure around 2 x 10⁻⁹ Torr. All samples are fixed using carbon tape and grounded to stainless steel stubs. The non-polarized samples are introduced in the spectrometer through an argon-filled glovebox and the polarized samples through a fast port with minimal ambient (ca. 5 min) and light exposure. The XPS binding energy scale is calibrated with sputter-cleaned Cu, Au, and Ag foils. The XPS spectra are processed using the CasaXPS software package (Casa Software Ltd). The raw XPS data undergo a Shirley background correction and all remaining core level peaks are fit

to known chemical components using a 70% Gaussian/30% Lorentzian line shape. In order to minimize random errors, relative peak shape, width and shifts are held constant, which is extremely important when multiple species are used to fit a single peak. Comparisons are made by calculating peak area ratios for each element considering their KE-dependent analyzer transfer functions and orbital cross sections, which is basically done by using the instrument-dependent relative sensitivity factors.

UPS (He I excitation at 21.22 eV, pass energy of 5 eV) spectra are acquired at a photoelectron takeoff angle of 90° (normal to the surface). The He discharge lamp (SPECS UVS 10/35, 25 mA) and a chamber pressure of 1 $\times 10^{-7}$ Torr using ultra high purity (UHP) He that is run through a liquid nitrogen-cooled trap to remove impurities. The sample is biased at -10.0 V to enhance the photoelectron yield at the low kinetic energy edge (LKE). The Fermi energy (E_F) is calibrated with sputter-cleaned Au.

S1.5.3 Ultraviolet-visible (UV-Vis) spectrophotometry

Absorbance data of the perovskite films were measured using an Ocean Optics Balanced Deuterium Tungsten Source (210-2500 nm) and an OCEAN-FX-XR1 fiber optic spectrometer (200-1025 nm) with a 25 μ m slit controlled with the Oceanview software package. The perovskite film spectra were collected relative to a bare ITO substrate.

S1.5.4 Electrochemistry

The perovskite film is evaluated using a three-electrode configuration using a gold film and an Ag/AgCl foil as a counter and reference electrode, respectively. All voltammograms were recorded using a CH Instruments Electrochemical Analyzer Model 660C potentiostat controlled with the corresponding software package. Prior to evaluating the perovskite devices, the redox probes were evaluated by cyclic voltammetry at different scan rates (10-500 mV s⁻¹ for 10 cycles) to determine

their mass transport and kinetic behavior in the solid electrolyte. Those redox probe test structures consisted of a solid electrolyte film with redox probe wrapped around an Ag/AgCl foil pressed in between two gold electrodes used as a counter and working electrode. These test device stacks were pressed and kept together using two thin metal plates tightened with four screws. All device structures were assembled and tested in ambient atmosphere.

S1.5.5 Spectroelectrochemistry

Potential-controlled (CH Instruments Electrochemical Analyzer Model 660C potentiostat) spectroelectrochemical measurements of perovskite films on ITO working electrodes (1 cm²) are recorded using the previously described three-electrode device configuration. The complete device, including the lead halide perovskite film, is placed in the path of the UV-vis spectrophotometer (Ocean Optics system as described above) and a background spectrum is taken after a fixed waiting period (t = 5 min) at a potential of -0.5 V vs Ag/AgCl where the perovskite is expected to show the optical and electrical properties of the as-deposited film. Steady-state absorption spectra are acquired after 5 min at defined potentials (20 mV intervals in the bleaching regime around the conduction band) between -0.5 V vs Ag/AgCl to -1.3 V vs Ag/AgCl using the bulk electrolysis feature in the control software.

S2 Additional Data for Band Edge Determination



Figure S1: Full valence band analysis with $\blacksquare = A(730 \text{ nm})$ (versus the baseline absorbance A(820 nm)) and $\blacktriangle = dA/dE$ in a potential range of -0.6 V to -0.9 V and -1.1 to -1.3 V with 0.1 increments and -0.9 to -1.1 V with 0.02 V increments, taken from in-situ spectroelectrochemical data for the bleaching of MAPbI₃ valence band for the stack in (a), with no redox probe, in ambient conditions (inset). The red line is a Gaussian fit with a maximum at 5.62 eV with an onset at 5.44 eV as a guide for the eye.



Figure S2: Characterization of frontier orbital energetics for MAPbI₃ with UPS. Onset in secondary edge is determined to be 14.7 eV in kinetic energy, or a work function of 4.8 eV. (Inset) Linear extrapolation of the HKE edge affords the estimation of the E_{VB} at 30.3 eV on the kinetic energy scale, or 0.8 eV below the Fermi level. Using a photon energy of 21.22 eV yields an ionization energy of 5.62 eV with respect to surface vacuum.



S3 Supplementary Note 1 - post-mortem characterization

Figure S3: Pb 4f, I 3d, N 1s and C 1s high-resolution XPS core level spectra of (top-to-bottom) an as-deposited MAPbI₃ film, a similar MAPbI₃ film after a solid electrolyte peel, and similar films after oxidation to 0.4 V and 0.8 V at 0° take-off angle.

In Figure S3, XPS Pb 4f, I 3d, N 1s, and C 1s core level spectra are recorded for the following, from top to bottom: i) an as-deposited near-stoichiometric MAPbI₃ film; ii) a similar MAPbI₃ film after a stick and peel with the SE (MAPbI₃ + [EMIM][TFSI]); iii) a similar MAPbI₃ film after oxidation to 0.4 V (\sim -5.1 eV wrt vacuum, within the band gap) which is representative of the region where we observe reduction of electrochemically-formed defects in Figure 4 of the main text; and iv) 0.8 V (\sim -5.4 eV, at the valence band edge) consistent with Q_{ox} region of Figure 4. We note the latter two samples also used the peel method to remove the electrolyte after poising at these applied potentials.

Table S1: Binding energies, FWHM, chemical origins and elemental concentration for all Pb 4f,	I
3d, N 1s and C 1s high-resolution core level spectra at 0° incident angle shown in Figure S3. Pb	, ^δ
refers to under-coordinated valence state of Pb, where $(0 \le \delta \le 2)$.	

sample	photoelectron	BE / eV	FWHM	chemical origin	elemental
					concentration
	Pb 4f _{7/2}	138.1	0.891	Pb^{II+}	9.97
	Pb 4f _{7/2}	136.6	0.891	Pb ^δ	0.64
	I 3d _{5/2}	619.1	1.061	I-	31.20
MAPbI ₃	N 1s	402.1	1.151	ammonium salt	12.20
U	C 1s	284.8	1.132	aliphatic carbon	25.94
		286.1	1.132	C-N	20.05
	Pb 4f _{7/2}	138.2	0.896	Pb^{II+}	2.25
	Pb 4f _{7/2}	136.6	0.896	Pb^{δ}	0.09
	I 3d _{5/2}	619.0	1.160	I-	6.40
	N 1s	401.6	1.277	ammonium salt	9.77
	0.1	399.3	1.277	N ⁻	3.11
MAPDI ₃ +	C Is	284.8	1.052	aliphatic carbon	6.55
peel and stick		286.2	1.052	C-N	17.75
electrolyte		286.8	1.052	N-C-C-N	6.55
		287.5	1.052	N-C-N	3.28
	F 1	293.1	1.000	C-F ₃	6.55
	F IS	689.1	1.740	C-F ₃	20.58
	S 2p _{3/2}	169.3	1.125	0-S-0	3.37
		532.9	1.564	0-S-0	13.72
	Pb $4f_{7/2}$	138.2	0.909	Pb ⁿ⁺	0.89
	Pb 4f _{7/2}	136.5	0.909	Pb ^o	0.12
	I 3d _{5/2}	619.1	1.11/	ľ	2.41
	N Is	402.0	1.366	ammonium salt	8.53
	0.1	399.5	1.084	N ⁻	3.57
MAPD13	C Is	285.0	1.224	aliphatic carbon	5.31
oxidized to		286.3	1.224	C-N	9.45
0.4 V		286.8	1.224	N-C-C-N	5.31
		287.3	1.224	N-C-N	2.66
		287.3	1.224	C-0	4.04
	F 1	293.0	1.224	C-F ₃	8.63
	F IS	689.0	1./16	C-F ₃	29.92
	S 2p _{3/2}	169.1	0.987	0-S-0	3.84
	<u> </u>	532.8	1.2/1	0-S-0	15.30
	Pb 4f _{7/2}	138.2	0.866	Pb ⁿ⁺	0.78
	I 3d _{5/2}	619.0	1.072	I ⁻	2.48
	N 1s	401.9	1.378	ammonium salt	9.39
		399.5	1.125	N-	4.00
	C 1s	284.9	1.150	aliphatic carbon	4.76
MAPbI ₃		286.2	1.150	C-N	11.09
oxidized to		286.8	1.150	N-C-C-N	4.76
0.8 V		287.3	1.150	N-C-N	2.38
		287.3	1.150	C-0	5.17
		293.0	1.150	C-F ₃	8.20
	F 1s	689.0	1.720	C-F ₃	28.95
	$S 2p_{3/2}$	169.0	0.995	0-8-0	3.66
	O_{1s}	532.8	1.329	O-S-O	14.39
	O IS	532.8	1.329	0-5-0	14.39

Complementary data for O1s and F1s core levels were also collected. In Figure S3, peaks are fit to known chemical components following a 70% Gaussian/30% Lorentzian line shape. The C 1s deconvolution is based on the N-C-N:C-N:N-C-C-N:C-C ratios, which are 1:2:2:1 in the EMIM cation. ^{S1} For the solid electrolyte peel, the C-C peak was based on the N-C-N peak area and carbon contamination. After oxidation, the C-C peak is reduced compared to the N-C-N contribution, which suggests formation of oxidized species so that the N-C-N peak is based on the C-C peak area and an extra C-O contribution. Table S1 provides peak assignments, relative binding energies, full width half maximums of the fitted peaks, and percent composition after correction for relative sensitivity factors for the XPS instrumentation as described above.

Table S2: Relative atomic ratios from Pb 4f, I 3d, N 1s and C 1s core level spectra for an asdeposited MAPbI₃ film, as a function of take-off angle in the XPS experiment (angle-resolved XPS, AR-XPS). The atomic ratios for Pb 4f core level spectra are calculated using Pb = Pb_{perovskite} + Pb^{δ}.

	ratio / 0º	ratio / 30°	ratio / 60º	expected ratio
I/Pb	3.13	3.02	2.44	3
Pb ⁸ /Pb _{perovskite}	0.06	0.09	0	-
N/Pb	1.22	1.19	1.12	1
C/N	1.64	1.55	1.48	1

Table S3: Relative atomic ratios from Pb 4f, I 3d, N 1s, F 1s, O 1s and C 1s core level spectra of an as-deposited MAPbI₃ film after stick and peel with the solid electrolyte, as a function of take-off angle in the XPS experiment (angle-resolved XPS, AR-XPS). The atomic ratios for Pb 4f core level spectra are calculated using Pb = Pb_{perovskite} + Pb^{δ}.

	ratio / 0º	ratio / 60°	expected ratio
I/Pb	2.84	3.18	3
Pb ⁸ /Pb _{perovskite}	0.04	0	-
F/O	1.49	1.45	1.5
F/C	3.14	2.54	3
O/C	2.09	1.75	2
N ⁻ /O	0.23	0.13	0.25
MA ^a /Pb	1.51	2.55	1

More detailed comparisons are described based on the calculation of the elemental ratios for all samples for AR-XPS spectra at 0°, 30° and 60° take-off angle in Tables S2-S5. First, the Pb/I ratio for the as-deposited MAPb₃ film shows a low surface iodide ratio, which suggests slow corrosion of iodide defects to gaseous I₂ leaving behind reduced, under-coordinated Pb^{δ}.^{S2} Here, δ refers to a valence state for lead that is greater than zero but less than two ($0 \le \delta < 2$). This is consistent with the observed PbI₂ signatures in the XRD and UV-vis data in Figure 2a and 2b of the main text. When we stick and peel the SE to/from the MAPbI₃, the absolute intensities of the Pb and I CL spectra are attenuated – a residual SE/IL film is left behind with a thickness estimated to be ca. 25 Å following

$$t = -\ln\left(\frac{I}{I_0}\right)\lambda\cos\theta \tag{S1}$$

with I_0 is the maximum intensity of element in the substrate, I is the maximum intensity of element in the substrate and top layer, t is the thickness, θ is the take-off angle normal to the surface and λ is the electron inelastic mean free path based on calculations in literature.^{S3,S4} The Pb/I elemental ratios at the surface are closer to those expected for as-deposited MAPbI₃, suggesting removal of a non-stoichiometric region from the as-deposited thin film. A near 1:1 EMIM/TFSI ratio is also observed using the N 1s, C 1s, and F 1s signatures in Table S1, and we propose that the post-peel residual ionic liquid thin film is interacting strongly enough with the nearly stoichiometric MAPbI₃ film to be retained, and could be stabilizing the surface (ex. stabilizing grain boundaries).

With the knowledge that the SE itself is not degrading the surface, we have created a reliable method to study electrochemical processes at the perovskite interface. For example, by matching the i/V curves in Figure 3c (panel i) with the calculated elemental ratios measured at the MAPbI₃ surface after controlled oxidation (observations only after the forward scan) gives clear evidence of iodide movement from the near-surface region to the bulk, as previously described.^{S5} Tables S4

and S5 show a reduction in the surface concentration of iodide. Indeed, the Pb/I ratio at 0° is highest for the film oxidized to 0.8 V. The oxidation process within the valence band might also explain the loss in Pb^{δ} species. We validate this band bending and ion migration mechanism with a direct link to the hole injection process in the CV in Figure 4a. Specifically, the electroactive defects are able to move to and from the perovskite/electrolyte interface depending on the electric field. From the MA/Pb ratio, we conclude that simultaneously MA cations at the interface are pushed into the electrolyte with almost none left at 60⁰ take-off angle. After oxidation, the 1:1 EMIM/TFSI ratio shifts due to an increase in the C-F₃ peak compared to the N-C-N and N-C-C-N contributions in the C 1s spectrum, indicating that the electric field pushes TFSI anions towards the MAPbI₃ surface. Contrarily, (N)-C-(C)-N contributions of EMIM cations decrease, which could suggest cations are either repelled at anodic potentials from the semiconductor surface and/or are located in a buried interface (ex. grain boundary). Lastly, this oxidation process in ambient conditions generates an extra C-O contribution in combination with a drop in C-C contribution. As gel was removed in ambient, we cannot conclude if the reaction is associated with the redox activity of the semiconductor with the gel or due to ambient gas reactions post gel removal. However, this contribution is low, and we can still conclude our electrochemical approach with photoelectron spectroscopy measurements has allowed us to do a detailed post-mortem characterization of these MAPbI₃ films under stress.

Table S4: Relative atomic ratios from Pb 4f, I 3d, N 1s, F 1s, O 1s and C 1s core level spectra of an as-deposited MAPbI₃ film oxidized to 0.4 V, as a function of take-off angle in the XPS experiment (angle-resolved XPS, AR-XPS). The atomic ratios for Pb 4f core level spectra are calculated using Pb = Pb_{perovskite} + Pb^{δ}.

	ratio / 0º	ratio / 30°	ratio / 60°	expected ratio
I/Pb	2.67	2.78	2.06	3
Pb ^δ /Pb _{perovskite}	0.13	0.22	0.15	-
F/O	1.95	2.02	1.99	1.5
F/C	3.47	4.05	2.91	3
O/C	1.77	2.01	1.46	2
N ⁻ /C	0.41	0.47	0.46	0.5
MA ^a /Pb	1.38	1.49	0.17	1

^{*a*} The contribution for MA is calculated by assuming a 2:1 N^+/N^- area ratio in the N 1s core level peak, which considers a 1:1 EMIM/TFSI ratio which is rough estimate.

Table S5: Relative atomic ratios from Pb 4f, I 3d, N 1s, F 1s, O 1s and C 1s core level spectra of an as-deposited MAPbI₃ film oxidized to 0.8 V, as a function of take-off angle in the XPS experiment (angle-resolved XPS, AR-XPS).

	ratio / 0º	ratio / 30°	ratio / 60º	expected ratio
I/Pb	3.20	2.16	2.07	3
F/O	2.01	1.83	1.99	1.5
F/C	3.53	2.55	2.91	3
O/C	1.75	1.39	1.46	2
N ⁻ /C	0.48	0.35	0.46	0.5
MA ^a /Pb	1.78	1.49	0.17	1

^{*a*} The contribution for MA is calculated by assuming a $2:1 \text{ N}^+/\text{N}^-$ area ratio in the N 1s core level peak, which considers a 1:1 EMIM/TFSI ratio which is rough estimate.

S3 Additional Electrochemical Data



Figure S4: Five consecutive cyclic voltametric scans of an over-stoichiometric (red) and nearstoichiometric (blue) MAPbI₃ film in contact with a solid electrolyte layer without a redox probe in ambient conditions focused on the iodide/triiodide redox process. The red curve is offset by 100 μ A.

	E ⁰ vs	E ⁰ vs	reaction	E _{ref} / V (in	references
	$Fc/Fc^+ / V$	Ag/AgCl / V ^a		$ACN)^b$	
$E^0(I_3^-/I_2^-)$	-0.6	-0.5	$I_3^- + e^- \leftrightarrow I_2^- + I^-$	<-0.95	Boschloo and Hagvelt ^{S6}
$E^{0}(I_{3}^{-}/I^{-})$	-0.1	0	$I_3^- + 2e^- \leftrightarrow 3I^-$	-0.25	Bentley et al. ^{S7}
$E^0(I_2^-/I^-)$	0.55	0.65	${I_2}^- + e^- \leftrightarrow 2I^-$	0.3	Wang et al. ^{S8}
$E^{0}(I^{-}/I^{-})$	0.8	0.9	$\mathrm{I}^- + \mathrm{e}^- \leftrightarrow 2\mathrm{I}^-$	0.6	Boschloo and Hagvelt ^{S6}
			$I_3^- + hv \leftrightarrow I_2^- + I^-$		Roy et al. ^{S9}

Table S6: Relevant redox potentials (vs Fc/Fc⁺ and Ag/AgCl QRE) of the iodide/triiodide redox system.

^{*a*} The pseudo reference electrode potential was calibrated against the formal potential of the IUPAC recommended Fc/Fc^+ process in the electrolyte of interest, taking into consideration the difference in the diffusion coefficients of Fc and Fc⁺.

 b An overall shift of +0.15 V vs Fc/Fc⁺ is seen in the solid electrolyte compared to the reference potential in acetonitrile.



Figure S5: Band diagram of MAPbI₃, PbI₂ and the Fc/Fc⁺ redox probe in combination with the CVs shown in Figure 3c.

S4 Supplemental Note 2 – Valence band electrochemistry

Defect quantification requires a systematic comparison in currents based on applied potential. To do this using cyclic voltammograms, we systematically increased the size of the potential window. We note all "endpoints" for cathodic potentials in this experiment were fixed at -0.5 V (vs. Ag/AgCl). A specific anodic "end potential" was set, starting first with 0.4 V vs. Ag/AgCl. In Figure 4 of the main text and in Figures S6a-c below, we conducted five consecutive cyclic voltammograms between cathodic and anodic end potentials. Then the anodic potential was increased by 50 mV, and the experiment was conducted again, for anodic end potentials from 0.4 to 0.9 V. The total cyclic voltammograms conducted was then 55 CVs, all at a scan rate of 0.05 V/s. We note that in the presence of the redox probe Fc within the solid electrolyte, no hysteresis was observed between the five consecutive CVs for each potential window, clearly indicating the analysis was not inducing additional defects other than what exists in the active layer. It is possible that some defects could have been passivated and/or slight changes the surface chemistry could have occurred prior to the cyclic voltammetry experiments, as indicated in Supplementary Note 1. Figures S6a-c below show three different ranges of potential windows, described as the anodic potential endpoints relative to the onset in the valence band (0.7 V vs Ag/AgCl):

- 1.) Above valence band anodic end potentials (0.4 to 0.5 V vs. Ag/AgCl): There is no observation of defect reduction and no observation of Fc^+ reduction.
- 2.) Near valence band anodic end potentials (0.5 to 0.7 V vs. Ag/AgCl): There is clear evidence of defect reduction on the cathodic sweep, but minimal observation of Fc⁺ reduction. A small Fc⁺ reduction peak is observed for the 0.7 V anodic end potential CV (green curve).
- 3.) Valence state oxidation (0.7 to 0.9 V vs. Ag/AgCl): Increasing the number of valence states that are oxidized shows a systematic increase in reduction current of Fc⁺ as well as a decrease in the reduction of defects.



Figure S6a: CVs as a function of anodic potential endpoints approaching $E_{VB,onset}$ (0.4 to 0.5 V), followed by cathodic sweep in presence of 1 mM Fc at 0.05 V/s in ambient.



Figure S6b: CVs as a function of anodic potential endpoints approaching $E_{VB,onset}$ (0.5 to 0.7 V), followed by cathodic sweep in presence of 1 mM Fc at 0.05 V/s in ambient.



Figure S6c: CVs as a function of anodic potential endpoints surpassing $E_{VB,onset}$ (0.7 to 0.9 V), followed by cathodic sweep in presence of 1 mM Fc at 0.05 V/s in ambient.

S6 Supplementary Note 3 - defect quantification

From Figures S6a-c and Figure 4 of the main text, the collective data indicates that oxidation includes charges (Q) extracted from three events, depending on potential: oxidation of defects ($Q_{ox,defects}$), oxidation of ferrocene ($Q_{ox,Fc}$) and oxidation of valence states ($Q_{ox,valence}$). From Figures S6a-c, defect oxidation occurs first (at lowest oxidation potentials), followed by oxidation of ferrocene and valence band states.

We note that one cannot assume that oxidation is purely reversible, but one can quantify the amount of carriers in the reductive waves (Q_{red}), which includes the reduction of defects ($Q_{red,defects}$) and reduction of ferrocenium ($Q_{red,Fc+}$) to approximate defects. In Figure 4b of the main text, we show one CV scan as measured in Figure 4 which includes color shading to highlight key regions of interest, including distinguishing between Faradaic and non-Faradaic contributions. In Figure 4b, the non-Faradaic charging in the perovskite band gap is indicated in white and is considered background current due to double-layer capacitive contributions. In the forward scan, surface defects are (ir)reversibly oxidized and are pinned¹ to Fc with the formation of Fc⁺ together in a single oxidation peak (Q_{ox} , green). Interestingly, in the reverse scan, reductive peaks appear as energy-separated cathodic peaks. Briefly, at low anodic potentials, Faradaic current is ascribed to defect reactions, most likely Γ oxidation events.

From Figure 4b, a fraction of the defects can be reversibly reduced in the cathodic sweep, assumed to be due to hole transfer from the valence band.^{S10} The shallow lying level of the defects is consistent with the defect tolerant MAPbI₃ energy diagram ($Q_{red,defects}$, blue), where the valence

¹ Fermi-level pinning refers to the equilibrium condition of a semiconductor surface which is different from the equilibrium condition in the bulk. This free surface, or interface, of the semiconductor contains a continuum of localized energy states within the band gap that are either occupied by electrons or empty. Because, in equilibrium, the Fermi level must be a constant throughout the semiconductor, the semiconductor bands bend at the surface.

band lies at 5.5 eV and the defect density is centered at 5.4 eV.^{S11,S12} When enough defects are generated, band bending occurs within the near-surface region of the perovskite and facilitates Fc reduction ($Q_{red,Fc+/Fc}$, magenta). For all CV scans, the total oxidation charge is higher compared to the individual contributions, which means that all extra charge is considered to be part of an irreversible oxidation process.

By shifting the maximum oxidation potential, $E_{ox,end}$, as shown in Figure 4a, all these individual Faradaic processes can be quantified by calculating the charge under the curve by integrating the current following (eq S1)

$$Q = \int_{t_0}^{t_1} i \, dt = \frac{\int_{V_0}^{V_1} i \, dV}{v}$$
(S2)

In Figure 4b, the calculated charge contributions are plotted as a function of $E_{ox,end}$ revealing very interesting relationships. In Figure S7, we show the residuals after fitting Q_{ox} and $Q_{red,Fc/Fe+}$ with an exponential fit and $Q_{red,defects}$ with a Gaussian distribution. In what follows, we explain the choice for these distributions. The oxidation process follows an exponential increase with potential, consistent with Marcus-Gerischer theory for n-type materials, where the exponential term originates from the assumption that the fluctuation of the solvent molecules or dipoles is assumed to behave like a harmonic oscillator. Shifting $E_{ox,end}$ continuously probes an increased number of defects are immediately reduced back in the reverse scan unless they pin to the Fc⁺ in the electrolyte. Indeed, around 0.7 V vs Ag/AgCl, generated defects pin to Fc⁺ causing a drop in the $Q_{red,defects}$ contribution, which eventually disappears, explaining the fitted Gaussian distribution. From the maximum, with the assumption of a dielectric constant of 18,^{S13} a carrier density of 2.8 x 10^{23} m⁻³, ^{S14,S15} and an estimate of the contact area (0.8 cm²), we calculate a depletion width of 9.23 x 10^{-6} cm using (eq S2)

$$t = \sqrt{\frac{2\varepsilon_r \varepsilon_0}{e} V_0 \frac{1}{N_D}}$$
(S3)

with dielectric constant ε_r , vacuum permittivity ε_0 , elemental charge e and built-in voltage V_0 for a device to measure carrier density N_D . We note that the carrier density depends on the MAI:PbI₂ precursor ratio and varies between 10^{14} to 10^{18} cm⁻³.^{S16,S17} Finally, we predict a defect density N_{defect} of 2.14 x 10^{17} cm⁻³ at 0.72 V using (eq S3)

$$N_{\text{defect}} = \frac{\text{number of defects}}{At}$$
(S4)

with the number defects = $Q_{red,defects}$ / e and area A. Because defects are pinning to Fc⁺to form Fc, this reduction process depends on the defects formed in the oxidation process, which explains why both redox reactions follow the same exponential distribution.



Figure S7: Residual plots of the exponential fit following $y = A x \exp(-x/t) + y_0$ for (a) Q_{ox} and (b) $Q_{red,Fc/Fc+}$ and following $y = A x \exp(-1/2 ((x-x_c)/w)^2) + y_0$ for (c) $Q_{red,defects}$.

References

- (S1) Höfft, O.; Bahr, S.; Himmerlich, M.; Krischok, S.; Schaefer, J. A.; Kempter, V. Electronic Structure of the Surface of the Ionic Liquid [EMIM][Tf₂N] Studied by Metastable Impact Electron Spectroscopy (MIES), UPS, and XPS. Langmuir 2006, 22, 7120–7123.
- (S2) Juarez-Perez, E. J.; Ono, L. K.; Maeda, M.; Jiang, Y.; Hawash, Z.; Qi, Y. Photodecomposition and Thermal Decomposition in Methylammonium Halide Lead Perovskites and Inferred Design Principles to Increase Photovoltaic Device Stability. *Journal of Materials Chemistry A* 2018, 6, 9604–9612.
- (S3) Tanuma, S.; Powell, C. J.; Penn, D. R. Calculations of Electron Inelastic Mean Free Paths.
 IX. Data for 41 Elemental Solids over the 50 eV to 30 keV range. *Surface and Interface Analysis* 2011, 43, 689–713.
- (S4) Seah, M.P.; Dench W.A., Quantitative Electron Spectroscopy of Surfaces. *Surface and Interface Analysis* **1979**, *1*, 2.
- (S5) Chen, Y.; Zhou, H. Defects Chemistry in High-Efficiency and Stable Perovskite Solar Cells. *Journal of Applied Physics* 2020, 128.
- (S6) Boschloo, G.; Hagfeldt, A. Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells. Accounts of Chemical Research 2009, 42, 1819–1826.
- (S7) Bentley, C. L.; Bond, A. M.; Hollenkamp, A. F.; Mahon, P. J.; Zhang, J. Electrochemistry of Iodide, Iodine, and Iodine Monochloride in Chloride Containing Nonhaloaluminate Ionic Liquids. *Analytical Chemistry* 2016, 88, 1915–1921.
- (S8) Wang, X.; Stanbury, D. M. Oxidation of Iodide by a Series of Fe(III) Complexes in Acetonitrile. *Inorganic Chemistry* 2006, 45, 3415–3423.
- (S9) Roy, J. C.; Hamill, W. H.; Williams, R. R. Diffusion Kinetics of the Photochemical and Thermal Dissociation-Recombination of Trihalide Ions. *Journal of the American Chemical Society* 1955, 77, 2953–2957.
- (S10) Bertoluzzi, L.; Lopez-Varo, P.; Jiménez Tejada, J. A.; Bisquert, J. Charge Transfer Processes at the Semiconductor/Electrolyte Interface for Solar Fuel Production: Insight from

Impedance Spectroscopy. Journal of Materials Chemistry A 2016, 4, 2873–2879.

- (S11) Even, J.; Pedesseau, L.; Jancu, J. M.; Katan, C. Importance of Spin-orbit Coupling in Hybrid Organic/Inorganic Perovskites for Photovoltaic Applications. *Journal of Physical Chemistry Letters* 2013, 4, 2999–3005.
- (S12) Xiong, L.; Guo, Y.; Wen, J.; Liu, H.; Yang, G.; Qin, P.; Fang, G. Review on the Application of SnO₂ in Perovskite Solar Cells. *Advanced Functional Materials* **2018**, *28*, 1–18.
- (S13) Samiee, M.; Konduri, S.; Ganapathy, B.; Kottokkaran, R.; Abbas, H. A.; Kitahara, A.; Joshi,
 P.; Zhang, L.; Noack, M.; Dalal, V. Defect Density and Dielectric Constant in Perovskite
 Solar Cells. *Applied Physics Letters* 2014, 105
- (S14) Zhao, T.; Shi, W.; Xi, J.; Wang, D.; Shuai, Z. Intrinsic and Extrinsic Charge Transport in CH₃NH₃PbI₃ Perovskites Predicted from First Principles. *Scientific Reports* **2016**, *7*, 1–8.
- (S15) Wang, Q.; Shao, Y.; Xie, H.; Lyu, L.; Liu, X.; Gao, Y.; Huang, J. Qualifying Composition Dependent p and n Self-doping in CH₃NH₃PbI₃. *Applied Physics Letters* 2014, 105.
- (S16) DeQuilettes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S. Impact of Microstructure on Local Carrier Lifetime in Perovskite Solar Cells. *Science* 2015, *348*, 683–686.
- (S17) Bi, C.; Shao, Y.; Yuan, Y.; Xiao, Z.; Wang, C.; Gao, Y.; Huang, J. Understanding the Formation and Evolution of Interdiffusion Grown Organolead Halide Perovskite Thin Films by Thermal Annealing. *Journal of Materials Chemistry A* 2014, *2*, 18508–18514.