SUPPORTING INFORMATION

Electrochemical Impedance Analysis of Perovskite-Electrolyte Interfaces

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Experimental

Perovskite deposition

Spin-coated $MAPbI_3$ (or SC-$MAPbI_3$) films were prepared using a solvent-solvent extraction approach. Briefly, 62 wt % of methyl ammonium iodide (MAI) and PbI_2 (1.2:1 molar ratio) was dissolved in a mixed solvent of n-methyl-2-pyrrolidone (NMP) and gamma-butyrolactone (GBL) with weight ratio NMP/GBL=7/3. Pre-clean FTO substrate was spin-coated with 100 µL precursor at 2000 rpm for 25 s, and transferred into vigorously stirred diethyl ether (DEE) bath for fast crystallization. Perovskite film was further annealed at 150 °C covered with a petri-dish for 15 min to remove the excess of MAI.

SC-$MAPbBr_3$ films were prepared using solvent engineering approach. 1 M of equal molar MABr and $PbBr_2$ was dissolved in a mixed solvent of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) with volume ratio DMF/DMSO=7:3. 100 µL precursor was spin coated at 4000 rpm for 35 s, 1 mL of toluene was drop on the spinning substrate at 20 s to facilitate crystallization. For SC-$FA_{0.85}Cs_{0.15}PbI_3$ films, same procedure is used with a precursor containing 0.85 M FAI, 0.15 M CsI and 1M PbI_2.

For sprayed (SP) films, 1:1:1 PbI_2:MAI:MACl, 1:1 MABr:PbBr, and 0.85:0.15:1 FAI:CsI:PbI_2 precursors were dissolved in 0.5 M in DMF for SP-$MAPbI_3$, SP-$MAPbBr_3$, and SP-$FA_{0.85}Cs_{0.15}PbI_3$ films, respectively. Sprayed films were deposited in ambient using a 60 kHz Sono-tek ultrasonic spray nozzle with a 1 W atomizing power and N_2 as the carrier gas. A programmable syringe pump fed solution to the nozzle head with a 0.1 mL/min infusion rate. The stationary nozzle was fixed 5 cm above a rastering stage with a 30 mm/s path speed and 10 mm between passes. 30 coats were applied to glass/FTO substrates with a 10 minute anneal after each 10 coats. Substrates were held at 75, 75, and 170 °C during spray deposition and 100, 105, and 170 °C during the post anneal for $MAPbI_3$, $MAPbBr_3$, and $FA_{0.85}Cs_{0.15}PbI_3$ film deposition, respectively.

Electrochemical measurements

The electrochemical measurements were taken using an electrochemical workstation (Potentiostat 283, Princeton Applied Research) with a three electrode configurations. Perovskite thin films deposited on FTO glass sever as working electrode (working area about 1 cm^2). Pt wire was used as counter electrode and the reference electrode was a silver wire immersed in 0.01 M $AgNO_3$ in acetonitrile connected to the cell via a 0.1 M $TBAPF_6$ in CH_2Cl_2 salt bridge. The three electrodes were immersed in an electrolyte composed of 0.1 M $TBAPF_6$ in CH_2Cl_2 and sealed in a close glass chamber to avoid solvent lost and keep the working area constant. The measurements were taken under dark condition.

Liquid junction solar cell fabrication

The cell assembly schematic is shown in figure S4. Perovskite thin films with thickness about 300 nm were deposited on FTO with 50 nm TiO_2 blocking layer. The compact TiO_2 blocking layer was deposited by spray pyrolysis at 450 ^oC using 0.2 M titanium diisopropoxide bis(acetylacetonate) 1-butanol solution, followed by 450 ^oC annealing for 1 h. Pt nanoparticle coated FTO glasses were used as counter electrodes. The perovskite and Pt electrodes were stacked together and separated by 300 μm Surlyn spacer using hot pressing. Redox electrolyte containing 0.1 mM Fc/Fc^+ and 0.1M $TBAPF_6$ in CH_2Cl_2 was filled in the two electrode cell through pre-drilled holes on the Pt electrodes.

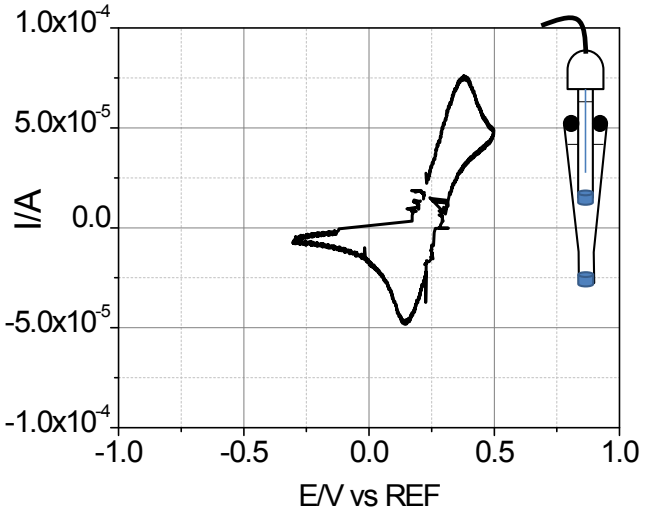


Figure S1. CV of Fc/Fc^+ with the composite electrode (illustrated on the right), $E_{1/2}$ = 0.25 V.

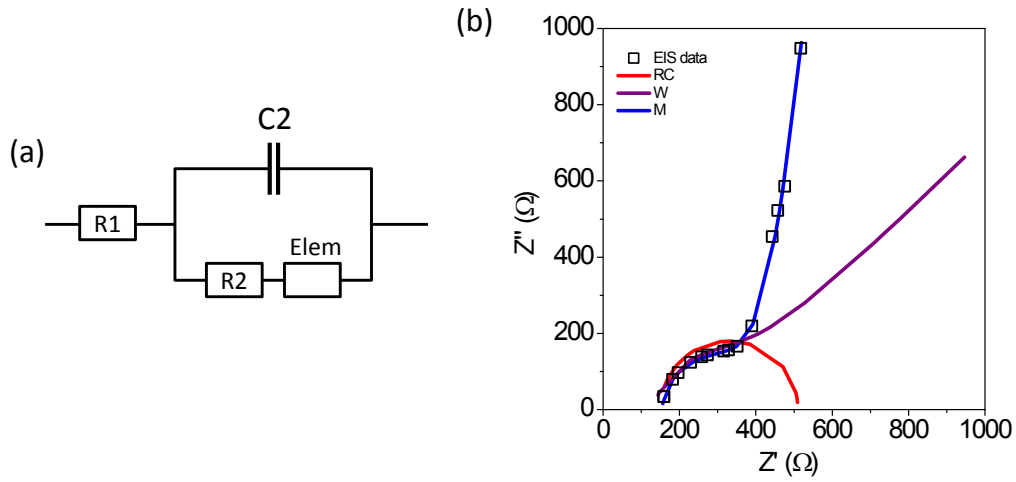


Figure S2. Equivalent circuits with different diffusion elements and fitting parameters for the SC-$MAPbI_3$ sample. RC denotes elem as just a connector; M denotes elem as an anomalous diffusion element; W denotes elem as a Warburg impedance.

Table S1. Fitting parameters of EIS plot of SC-$MAPbI_3$ in Figure S2 (above).

Diffusion element	**R1** **Ω**	**C2** **F**	**R2** **Ω**	**Diffusion element parameters**			
				s2 $\Omega\ s^{-1/2}$	**R3** Ω	**t3** **s**	a3
RC	150	8E-5	360	-	-	-	-
Warburg	150	3E-5	200	9090	-	-	-
Anomalous	150	5E-5	240		700	4E-3	0.6

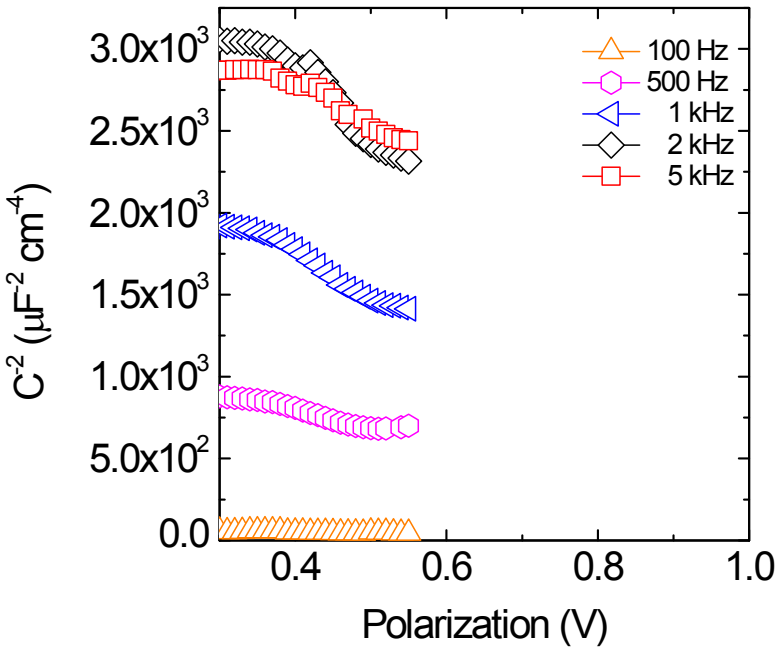


Figure S3. Dispersion of the MS plots for the spray-deposited SP-$MAPbI_3$ film.

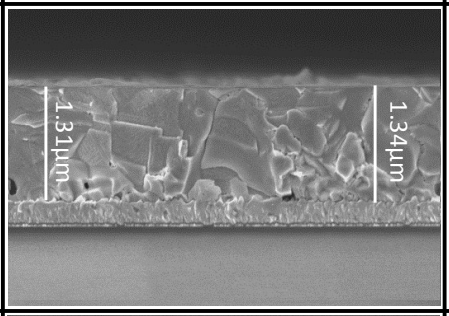
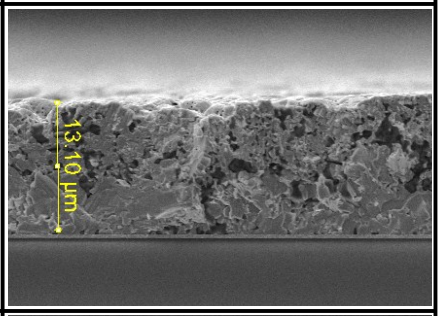
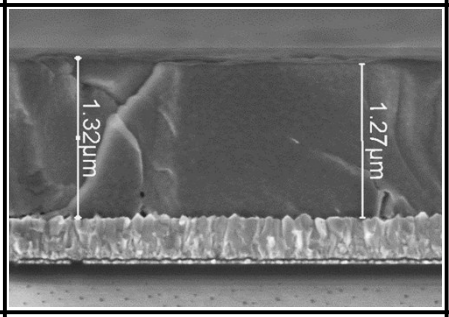
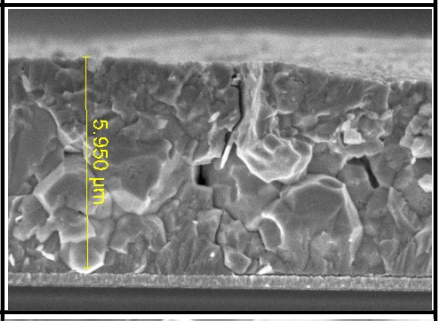
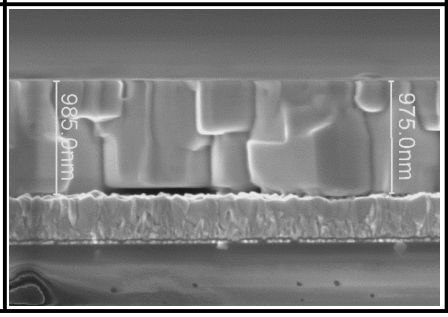
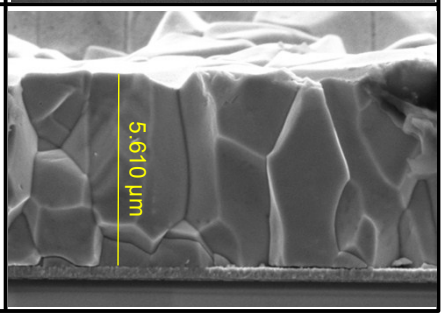
Compositions	Spin-coated (SC)	Spray-deposited (SP)
$MAPbI_3$		
$FA_{0.85}Cs_{0.15}PbI_3$		
$MAPbBr_3$		

Figure S4. Scanning electron microscopy images of cross section of perovskite films

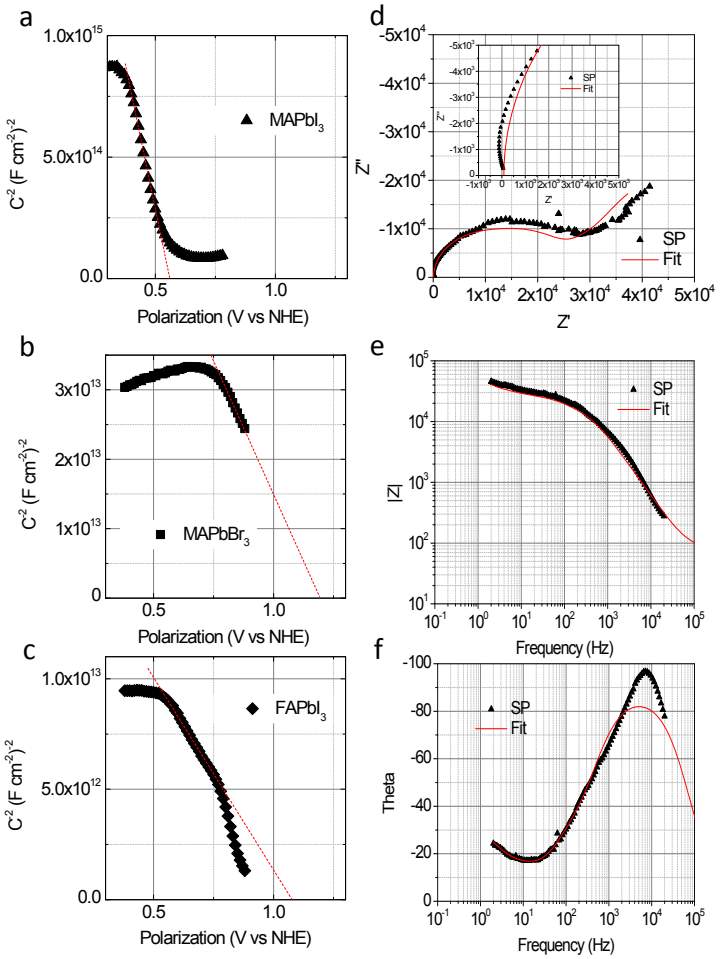


Figure S5. Characteristics of the spray deposited (SP) films, Mott-Schottky plots of (a) SP-$MAPbI_3$, (b) $MAPbBr_3$, and (c) $FAPbI_3$ at 1 kHz. EIS of SP-$MAPbI_3$ (d) Nyquist, (e) and (f) Bode plots.

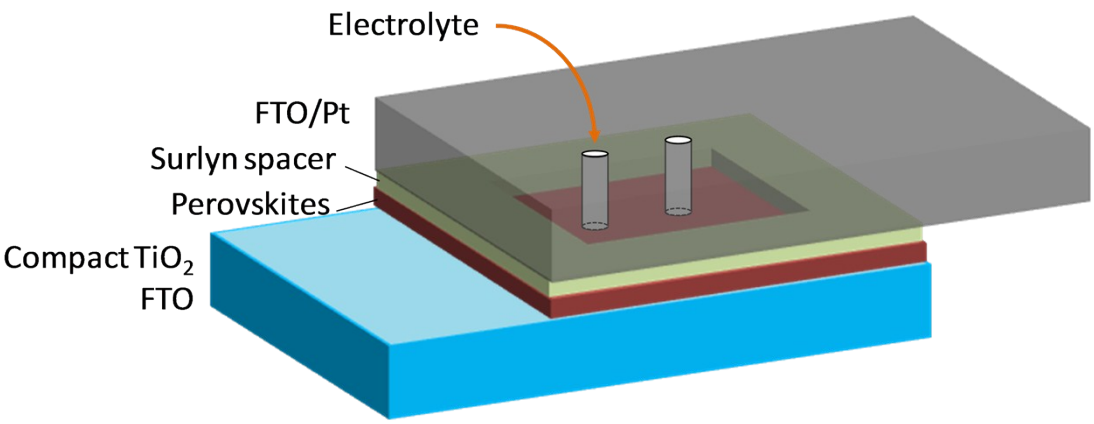


Figure S6. Schematics of assembly of perovskite liquid junction solar cells.

Table S2. Flat band potentials for various film compositions and deposition methods.

	Sample	V_{FB} (V vs NHE)
Spin coating (SC)	$MAPbI_3$	0.67
	$FA_{0.85}Cs_{0.15}PbI_3$	0.96
	$MAPbBr_3$	1.09
Spraying (SP)	$MAPbI_3$	0.56
	$FAPbI_3$	1.05
	$MAPbBr_3$	1.21

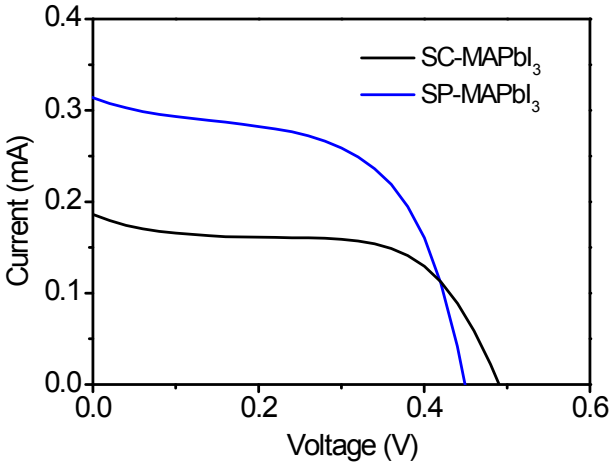


Figure S7. I-V curves of MAPbI3 liquid junction solar cells with films prepared by different methods.

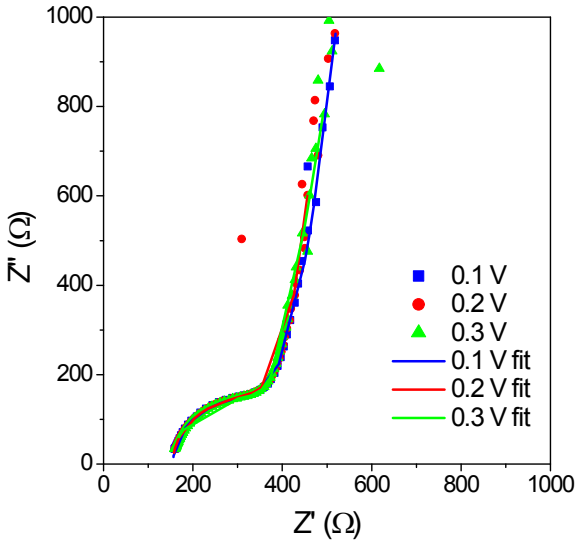


Figure S8. Nyquist plots of the SC-$MAPbI_3$ sample at various applied potential.

Table S3. Fitting parameters of the equivalent circuit to the Nyquist plots in figure S8 (above).

Applied potential (V vs. ref)	R1 Ω	C2 F	R2 Ω	Anomalous diffusion element		
				R3 Ω	t3 s	a3
0.1	150	5E-5	240	700	4E-3-	0.6
0.2	150	5E-5	245	552	3E-3	0.6
0.3	150	5E-5	264	300	2E-3	0.6

Figure S9. Photos of perovskite film soaked in DCM-based electrolyte.