Supporting Information

The Curious Case of Ion Migration in Solid-state and Liquid Electrolyte-based Perovskite Devices: Unveiling the Role of Charge Accumulation and Extraction at the Interfaces

Priya Srivastava[†, ^], *Ramesh Kumar*[†, ^], *Monojit Bag*[†, ‡, *]

† Advanced Research in Electrochemical Impedance Spectroscopy Laboratory (AREIS), Indian Institute of Technology Roorkee, Roorkee 247667, India

‡ Centre of Nanotechnology, Indian Institute of Technology Roorkee, Roorkee 247667, India

Corresponding author: monojit.bag@ph.iitr.ac.in

^ These authors contributed equally.

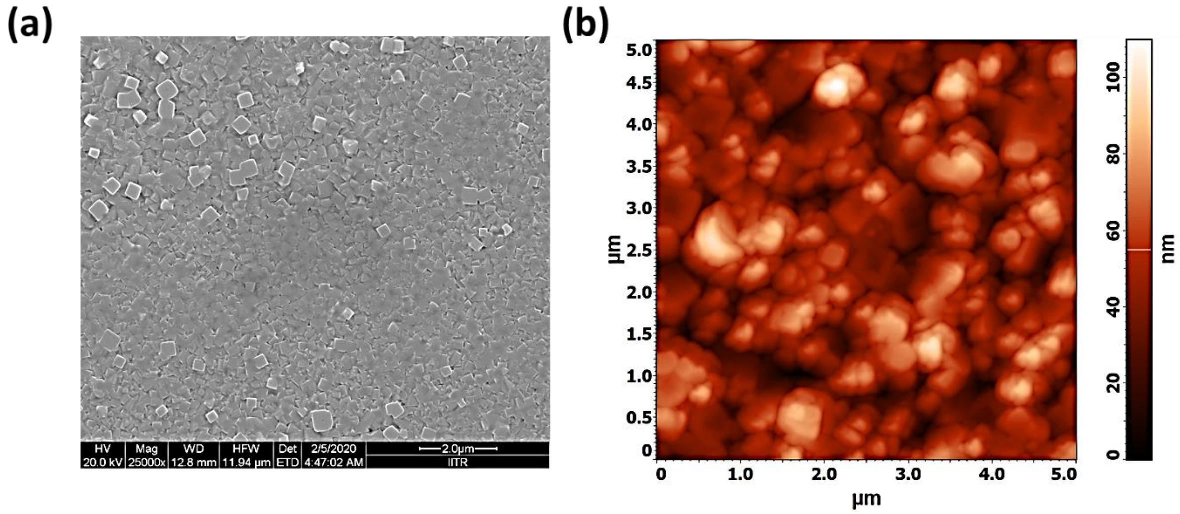

Figure S1: Top-view FESEM image and AFM image of the $CH_3NH_3PbBr_3$ film.

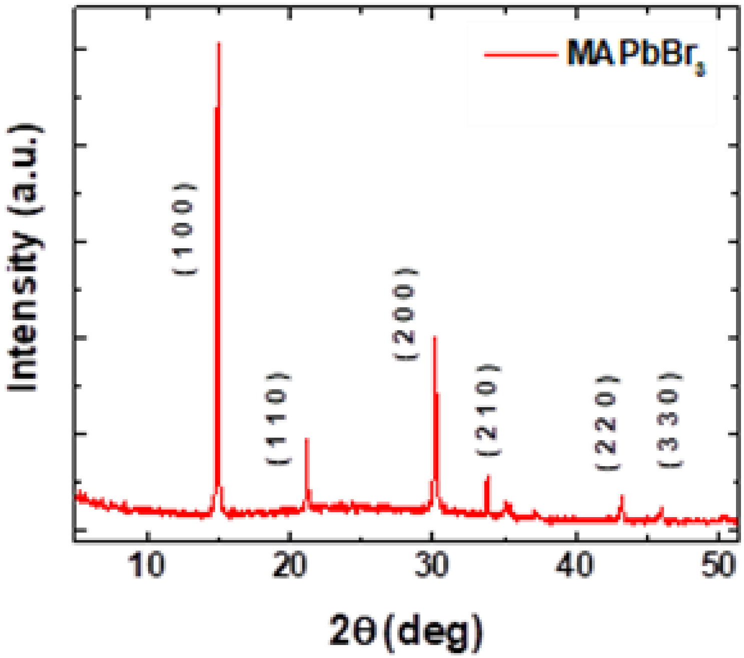

Figure S2: X-ray diffraction pattern of the $CH_3NH_3PbBr_3$ film.

Figure S3: Photographs of the S-S and L-E devices. Electrochemical cell was fabricated by placing a PDMS stamp with a hole to hold the electrolyte during the measurement.

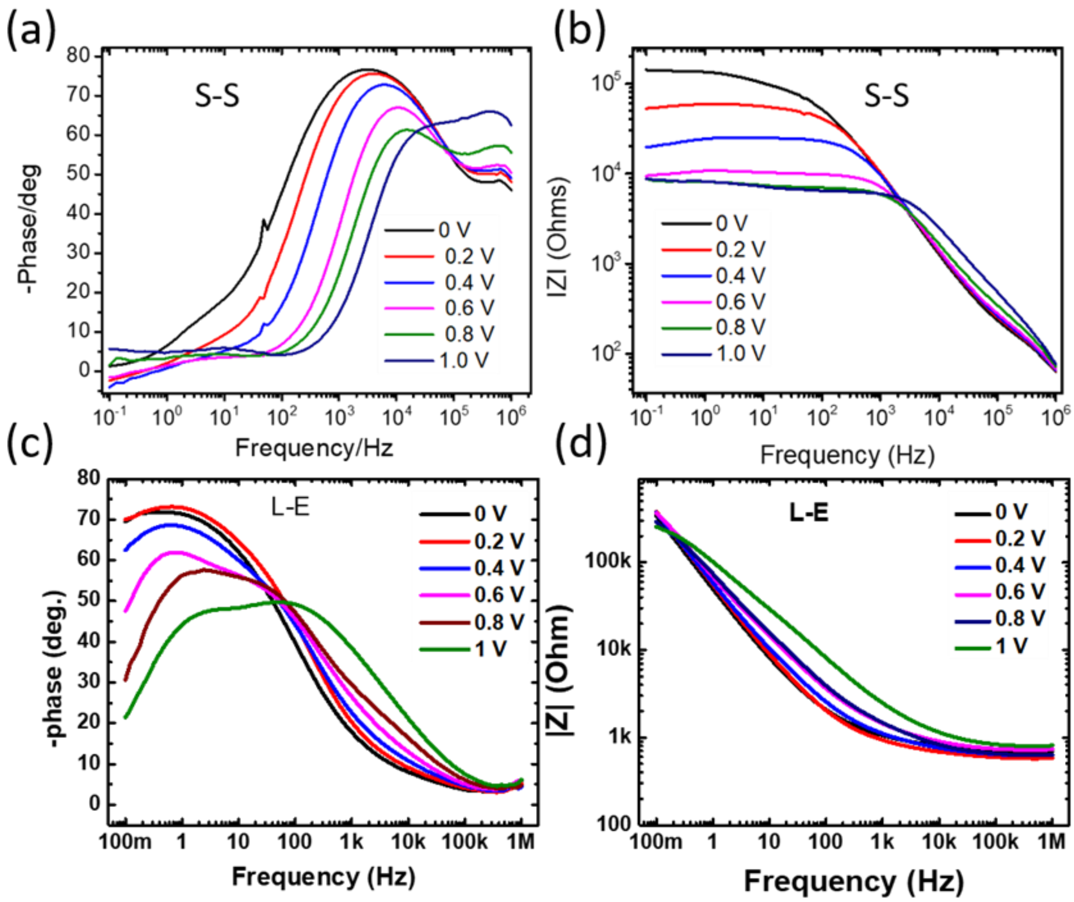

Figure S4: Bode plots of the perovskite-based device in solid-state (S-S) (a, b) geometry and liquid-electrolyte (L-E) (c, d) geometry.

Table S1: EEC fitting parameters for LE devices

Applied Voltage (V)	**0**	**0.2**	**0.4**	**0.6**	**0.8**	**1**
Chi-Sqr	0.000529	0.000413	0.00064	0.000776	0.00055	0.0001
Sum-Sqr	0.10629	0.083031	0.12871	0.156	0.11063	0.020178
R1(+)	2.74E-07	2.74E-07	2.74E-07	2.74E-07	2.74E-07	2.74E-07
R2(+)	683.1	578	624.4	738.4	631.7	778.4
CPE1-T(+)	2.36E-11	2.45E-11	2.19E-11	2.56E-09	2.28E-09	1.68E-11
CPE1-P(X)	1	1	1	0.7	0.7	1
R3(+)	1006	1078	2237	6738	5612	10091
CPE2-T(+)	1.22E-05	1.39E-05	1.03E-05	6.81E-06	7.00E-06	3.30E-06
CPE2-P(X)	0.7	0.7	0.7	0.7	0.7	0.7
R4(+)	282.1	283.2	441	804.3	1082	1828
R5(+)	4.34E+06	5.12E+06	2.01E+06	8.36E+05	4.10E+05	3.41E+05
CPE4-T(+)	3.22E-06	2.56E-06	2.37E-06	1.98E-06	1.64E-06	1.30E-06
CPE4-P(+)	0.84808	0.86431	0.85615	0.84661	0.83661	0.69688
CPE3-T(+)	1.15E-06	1.32E-06	1.48E-06	1.37E-06	1.50E-06	1.21E-06
CPE3-P(+)	0.76531	0.75927	0.7368	0.74103	0.7134	0.68456

Table S2: EEC fitting parameters for SS devices

Applied Bias (V)	**0.0**	**0.2**	**0.4**	**0.6**	**0.8**	**1.0**
Rs (Ω)	29.97	27.59	26.92	24.38	21.78	22.18
R1 (Ω)	95.59	110.2	128.4	162.6	222	227
R2 (Ω)	10266	43564				
R3 (Ω)	86724	11283	20879	9806	6759	6160
R4 (Ω)	44703	5781	3893	787.9	1544	2359
CPE1-T (F)	2.13E-8	2.78E-08	3.52E-08	5.52E-08	5.12E-08	2.30E-08
CPE1-P	0.90	0.88	0.86	0.82	0.83	0.90
CPE2-T (F)	7.2E-8	3.38E-08				
CPE2-P	1	0.91				
CPE3-T (F)	6.5E-8	1.50E-06	3.58E-08	3.12E-08	3.01E-08	1.73E-08
CPE3-P	0.86	0.73	0.89	0.90	0.89	0.90
CPE4-T (F)	1.4E-6				7.79E-05	4.63E-05
CPE4-P	.80				0.70	0.70
L (H)		2894	1748	312.1		

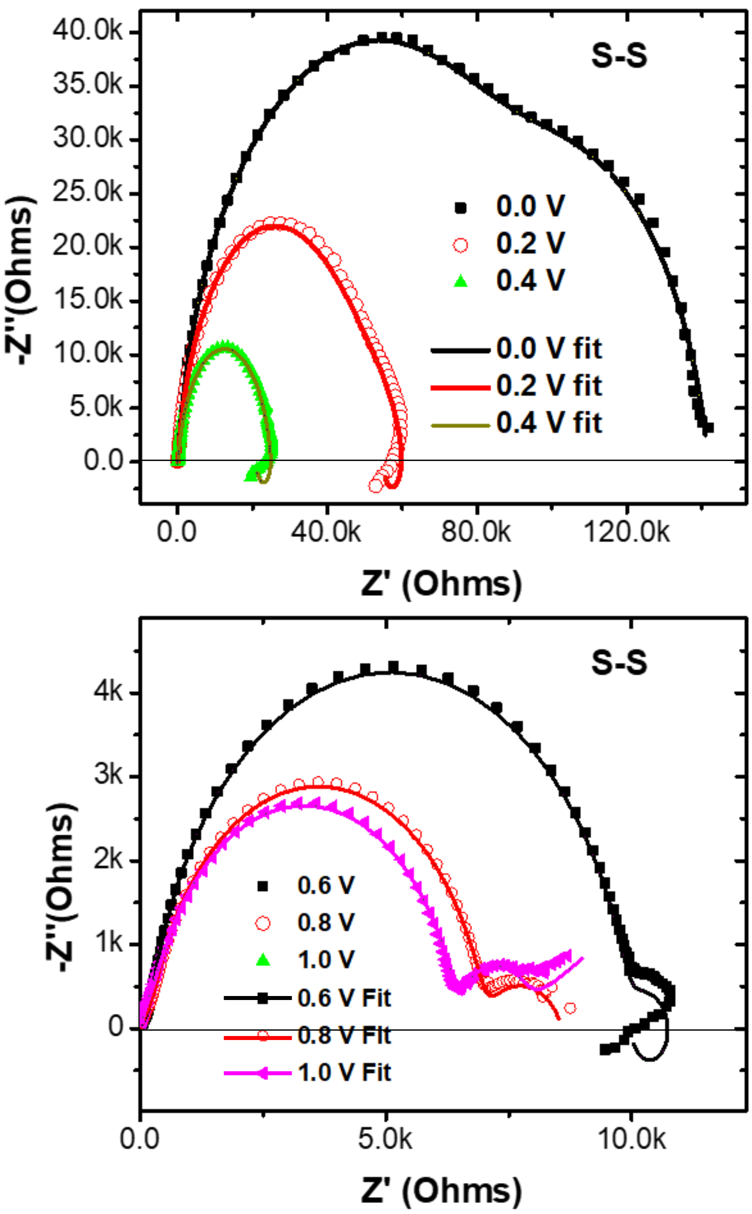

Figure S5. EIS Nyquist experimental data with corresponding fitting of S-S devices at different applied bias.

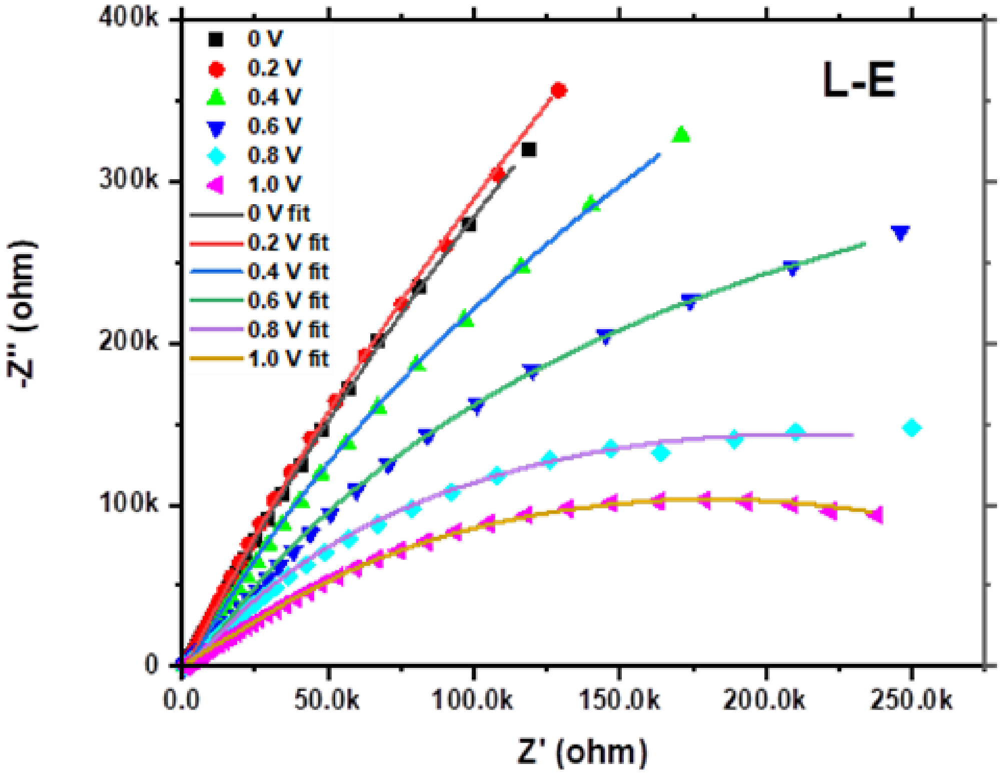

Figure S6. EIS Nyquist experimental data with corresponding fitting of L-E devices at different applied bias.

Dielectric properties and ionic conductivity

The dielectric properties of the hybrid perovskite devices (S-S, L-E) can be defined in terms of the complex permittivity $\varepsilon(\omega)$.[2,3]

$$\varepsilon(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \quad (1)$$

Where, $\varepsilon'(\omega)$ is the real part of the complex permittivity and $\varepsilon''(\omega)$ is the imaginary part of the complex permittivity represents the energy loss which can be expressed from the impedance spectra using the following relations:

$$\varepsilon'(\omega) = \frac{Z''}{\omega C_0\left(Z'^2 + Z''^2\right)} \quad (2)$$

$$\varepsilon''(\omega) = \frac{Z'}{\omega C_0\left(Z'^2 + Z''^2\right)} \quad (3)$$

Where, $C_0(= \varepsilon_0 A/d)$ is the vacuum capacitance, ε_0 is the free space permittivity, A is the area of the device/electrode and d is the thickness of perovskite film in both S-S and L-E devices.

To elucidate the ion migration in S-S and L-E devices, we have calculated the ionic conductivities by the Jonscher power law (JPL), according to following equation

$$\sigma_{tot.} = \sigma_{dc} + \sigma_{ac} = \sigma_{ele} + A_{ion}\omega^{n} \quad (7)$$

Where, the frequency-independent first term is electronic dc conductivity (σ_{ele}) arising owing to the electronic contribution in mixed electronic-ionic semiconductors. However, the last term is the ionic conductivity ($\sigma_{ion} = A_{ion}\omega^{n}$). In case of perovskite devices, the ionic conductivity can be calculated from Jonscher's law via equation $\sigma_{ion} = \varepsilon_0 \varepsilon'' \omega$.

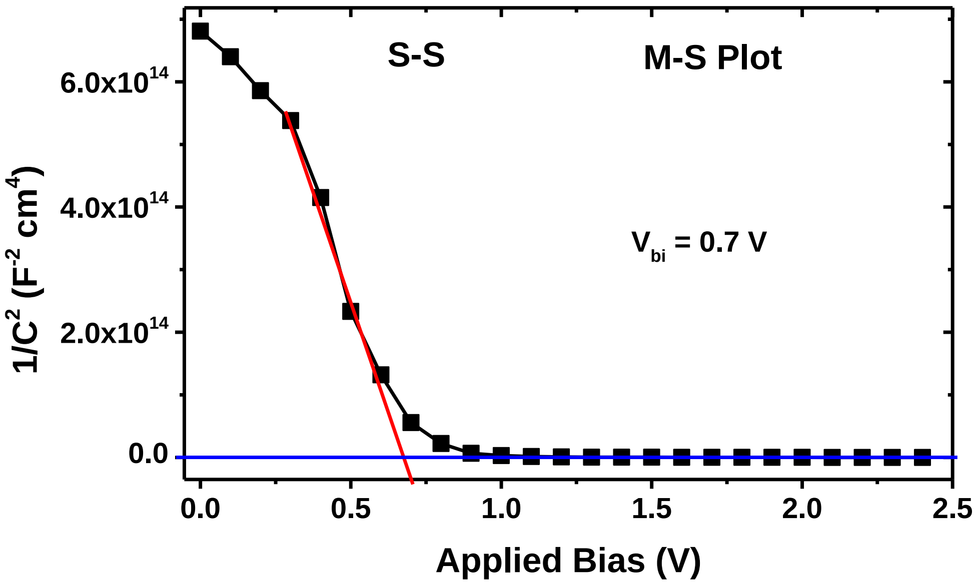

Figure S7: Mott–Schottky plot of the S-S device under dark.

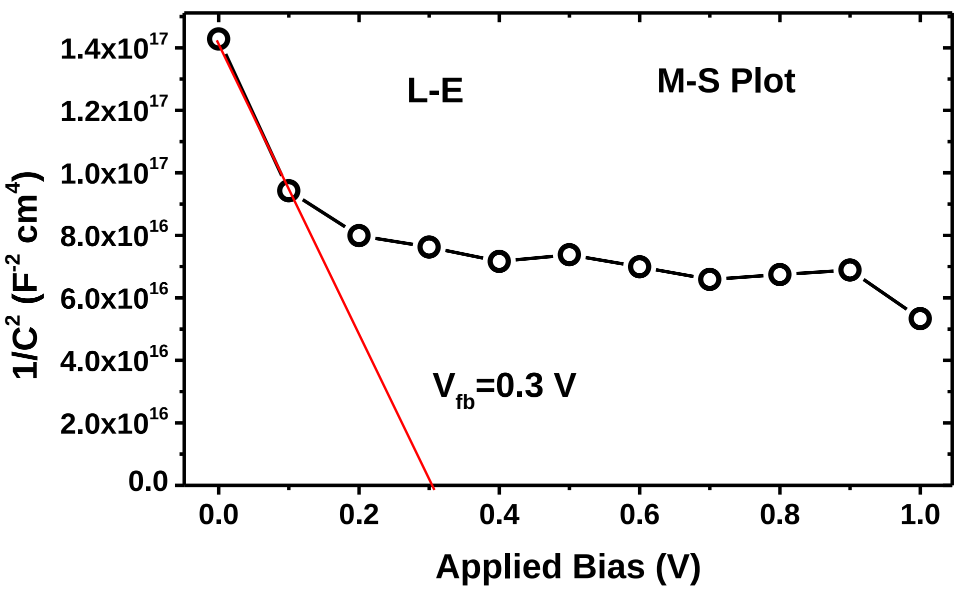

Figure S8: Mott–Schottky plot of the L-E device under dark.

References

(1) Kumar, R.; Kumar, J.; Srivastava, P.; Moghe, D.; Kabra, D.; Bag, M. Unveiling the Morphology Effect on the Negative Capacitance and Large Ideality Factor in Perovskite Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2020**, *12* (30), 34265–34273. https://doi.org/10.1021/acsami.0c04489.

(2) Kumar, R.; Srivastava, P.; Bag, M. Role of A-Site Cation and X-Site Halide Interactions in Mixed-Cation Mixed-Halide Perovskites for Determining Anomalously High Ideality Factor and the Super-Linear Power Law in AC Ionic Conductivity at

Operating Temperature. *ACS Appl. Electron. Mater.* **2020**, acsaelm.0c00874. https://doi.org/10.1021/acsaelm.0c00874.

(3) Srivastava, P.; Kumar, R.; Bag, M. Discerning the Role of an A-Site Cation and X-Site Anion for Ion Conductivity Tuning in Hybrid Perovskites by Photoelectrochemical Impedance Spectroscopy. *J. Phys. Chem. C 0* (0), null-null. https://doi.org/10.1021/acs.jpcc.0c09443.

(4) Srivastava, P.; Bag, M. Elucidating Tuneable Ambipolar Charge Transport and Field Induced Bleaching at the CH3NH3PbI3/Electrolyte Interface. *Phys. Chem. Chem. Phys.* **2020**, *22* (19), 11062–11074. https://doi.org/10.1039/d0cp00682c.