

Ruddlesden-Popper 2D Perovskite-MoS₂ Hybrid Heterojunction Photoelectrodes for Efficient and Scalable Photo-Rechargeable Li-Ion Batteries

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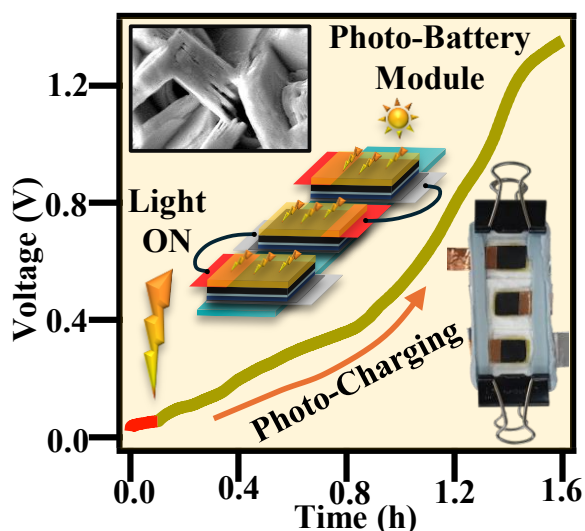


Photo-rechargeable batteries (PRBs) can provide a compact solution to power autonomous smart devices located at remote sites which cannot be connected with the grid. In this chapter, I have shown RP perovskite (BA)₂(MA)_{n-1}Pb_nI_{3n+1}, n=4 and MoS₂ hybrid heterojunction-based photoelectrodes for Li-ion PRB applications. Hybrid Li-PRB has achieved an average dark discharge specific capacities of 128.66 mAhg⁻¹ (capacity retention: 96.56 %) which enhanced to 180.67 mAhg⁻¹ under illumination (capacity retention: 97.39 %; photo-enhancement: 40.42 %) at 64 mAg⁻¹. Excellent performance of hybrid Li-PRB is attributed to the formation of type-II heterojunction which leads to improved crystallinity and film morphology. Our PRB has demonstrated a high PC-SE of 0.52 % under standard 1 Sun illumination, which outperforms other previously reported MHP based PRBs. This work provides a novel approach of harnessing the potential of MHPs for PRBs and offers new avenues for MHP photoelectrode for various applications beyond PRBs.

5.1 MHPs based PRBs

The development of standalone energy harvesting, and storage systems is essential to meet the power requirements at the off-grid locations for high power applications such as charging of electric vehicles (EVs) or for low power applications such as standalone sensors and other autonomous devices [Hu et al., 2019; Xu et al., 2015]. Currently, to accomplish this task, the solar cells are used to harvest the solar energy and due to the intermittent nature of sunlight the solar energy is stored in the batteries for later use. This combination of photovoltaic (PV) and energy storage devices help in the alleviation of energy poverty but provides very bulky and expensive solution, due to the use of complex and multiple electronic components, duplication of electrodes, additional space requirements, use of various materials in these two very different devices etc [Hu et al., 2019; Paolella et al., 2017; Xu et al., 2015]. To address these concerns, in 2018 Shahab et. al. reported the first PRBs based on 2D metal halide perovskite $(\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ as single active material to harvest solar energy and store the Li-ions in perovskite photoelectrode simultaneously [Ahmad et al., 2018]. In these PRBs, fluorine-doped tin-oxide (FTO) with prolonged Copper foil is employed as a transparent current collector electrode to couple light and transport photo-generated electrons to Cu foil from 2D perovskite via PCBM/rGO which worked as electron transport materials (ETM). I mentioned photo conversion and storage efficiency (PC-SE) of $\sim 0.034\%$ under 1 Sun illumination. Given the fact that these two-electrode based PRBs provided a proof of concept to achieve compact energy solutions, but the PC-SE and electrochemical performance of these PRBs require significant improvement to enable their commercialization for any real applications. Subsequently, in 2021 Neha et al. developed a Li-PRBs using lead-free bulk inorganic perovskite $\text{Cs}_3\text{Bi}_2\text{I}_9$ as active material and reported the PC-SE of 0.43% and 0.071 % with carbon felt and FTO based current collector electrode respectively [Tewari et al., 2021]. In 2022 Chen et. al published a Li-PRBs using DAPbI perovskite as photoactive material showing PC-SE of 0.49% [Chen et al., 2022a]. After using 30% carbon nanotube as a conducting additive and enclosing the Li-ion battery in a glass bottle, the reported device has degraded by $\sim 75\%$ galvanostatically after 20 cycles compared to its initial cycle. Moreover, rate cycling has not performed, and photo response is recorded in a small window (1.97-2.17 V). These are the major drawbacks in the commercialization point of view. In addition to PRBs, in 2022 Ramesh et. al published a photo-rechargeable supercapacitor using MAPbI_3 as an active material and demonstrating 0.02% OCV charging conversion efficiency [Kumar et al., 2022]. Recently, in 2023 Hongmin et al. reported two-electrode Zn-ion PRB based on Janus-jointed $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Te}$ which has shown PC-SE of $\sim 0.31\%$ [Liu et al., 2022]. The reported photoelectrode is composed of dual-active materials. Where $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite acts as solar energy harvesting material and Te particles as energy storage material, together forming the Janus structure. In addition to MHP, researchers have also explored other inorganic photoactive materials such as VO_2 , V_2O_5 , Fe_2O_3 , LiV_2O_5 , MoS_2 etc to develop a variety of photo-batteries based on Li/Zn-ion, [Boruah et al., 2021a; Chamola et al., 2023; Kumar et al., 2021; Salunke et al., 2022; Wang et al., 2022] redox flow, [Yan et al., 2013] lithium-air, [Liu et al., 2015; Lv et al., 2021] and aqueous rechargeable chemistries [Xie et al., 2021]. Though these recent developments have shown impressive device configurations and decent progress in the PC-SE of these MHP based PRBs. However, the reported capacity retention of these MHP PRBs shown decay which are majorly attributed to: (i) degradation of photoelectrode materials in the liquid electrolyte environment, (ii) prolonged exposure to intense light and (iii) change in optical properties of active material as a function of the state of charge.

Most of the above-mentioned issues are related to the structural and morphological properties of the MHPs, which may be improved by exploring the nanocomposite of MHP and inorganic nanomaterials etc [Cho et al., 2021]. Among these, for PRB applications the most promising strategy would be to explore the nanocomposites of quasi-dimensional MHPs with inorganic nanomaterials as these additives do not suffer from degradation issues in liquid electrolytes and are known to stabilize the structural properties of MHPs. For instance, the addition of MoS_2 nanoflakes in the MHP precursor solution trigger the heterogeneous nucleation of perovskite crystals and results in the overall improvement of structural, morphological, and optoelectronic properties of perovskites [Ahmad et al., 2015; Chandrasekar et al., 2019; Liu et al., 2020]. As I mentioned in chapter 3, I have shown $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ ($n=4$) and MoS_2 BHJ based photodetector has shown remarkable improvement in the photocurrent properties of the RP perovskite resulting in a maximum

photocurrent density of $\sim 9.8 \mu\text{A cm}^{-2}$, which is ~ 17 times higher than the reference device ($0.6 \mu\text{A cm}^{-2}$) and long cycling transient photo current under laser light ($\lambda_{\text{ex}} \sim 405 \text{ nm}$) showed reduction of 9.6 % in the peak photocurrent density after 200 cycles, while the pristine device degraded by ~ 39 % after 50 cycles [Ansari et al., 2023a]. Such improved photo-stability and optoelectronic properties offered by the RP perovskite-MoS₂ hybrids make them a potential system worth exploring for the PRBs.

5.2 Composition of hybrid electrodes for Li-PRB

Hybrid electrode contains RP perovskite (85 wt %) and MoS₂ nanoflakes (0.4 wt %). Moreover, super-P (3 wt%) and rGO (5 wt %) served as carbon additives and PVDF (7 wt %) is used as a binder. 20 μl (1.7 mg of perovskite) slurry is casted on FTO current collector and dried at 70 °C inside glove box for whole night to remove NMP solvent. The fabrication process for Li-PRBs are detailed in the Section 2.14 of chapter 2.

5.3 Device configuration of hybrid Li-PRBs

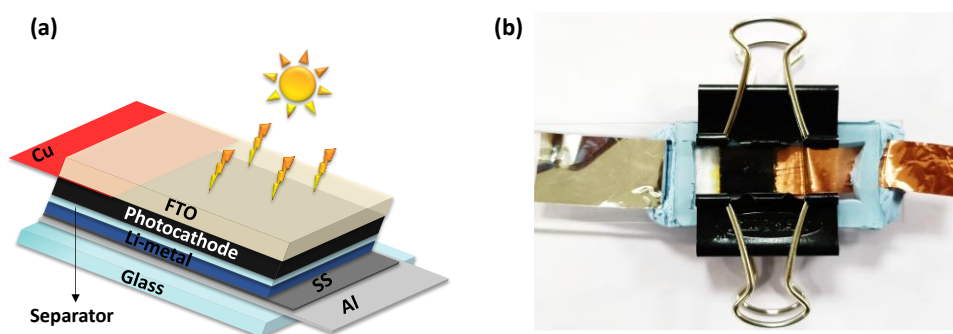


Figure 5.1 Schematic diagram for hybrid Li-PRBs. (b) Digital camera image for hybrid Li-PRBs.

Figure 5.1a shows the schematic diagram for hybrid Li-PRBs where, the solar illumination is coupled to the RP perovskite via FTO substrate which is connected with Cu-metal foil and acting as photoelectrode. Moreover, Al foil coupled with Li-metal serves as counter electrode. After placing different components of Li-PRBs systematically, it is sealed with Blu Tack glue and clip as shown in the camera image (**Figure 5.1b**). The detailed fabrication process is mentioned in **Sub-Section 2.14.2** of **Chapter 2**.

5.4 UPS spectra for RP perovskite material (BA)₂(MA)_{n-1}Pb_nI_{3n+1} (for n=4) and MoS₂

The electronic band position of n=4 and MoS₂ was investigated using UPS measurements (**Figure 5.2a-e**). The work functions (ϕ) were calculated from the difference between the cutoff of the highest binding energy and the incident photon energy (21.2 eV), which were estimated to be 3.73 eV and 3.70 eV respectively from the fermi level. Additionally, valence band maxima (VBM, E_v) were calculated from the cutoff of the lowest binding energy, which were found to be ~ 0.21 eV (for n=4) and ~ 1.0 eV (for MoS₂) from the fermi level. Based on these values and energy bandgap values ($E_g = 1.94$ eV for n=4 and $E_g = 1.58$ eV for n=MoS₂; these energy bandgap values are calculated in **Sub-Section 3.6.1** of **chapter 3** using Tauc's plot), the CBM (E_c) is obtained and energy scheme for pristine RP perovskite (n=4) and MoS₂ thin films is prepared which has shown the formation of a type II heterojunction between perovskite and MoS₂. These heterostructures are investigated for energy storage materials due to their efficient charge transport capability, faster kinetics, and electrochemical stability.

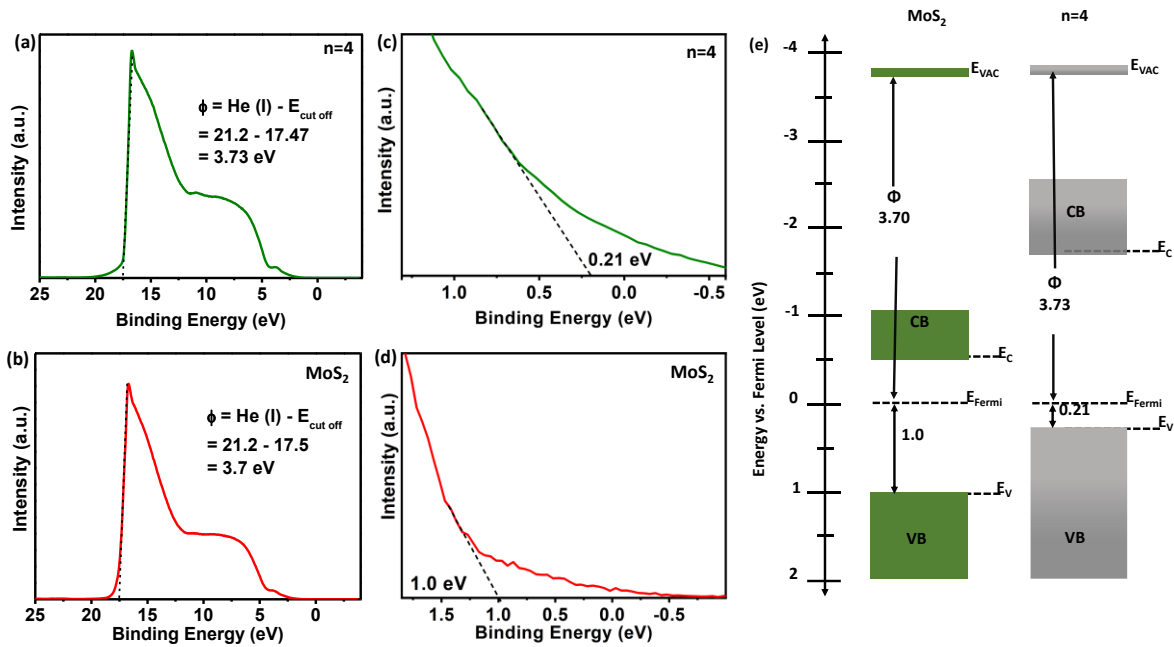


Figure 5.2 UPS spectra showing the secondary electron cut-off (onset) region for (a) pristine RP perovskite (n=4) and (b) MoS₂ nanoflakes. Valence band (VB) spectra for (c) pristine RP perovskite (n=4) and (d) MoS₂ nanoflakes. (e) Energy scheme for pristine RP perovskite (n=4) and MoS₂ nanoflakes with respect to the Fermi energy (E_{Fermi}). E_{VAC} , ϕ , E_{V} and E_{C} are representing the energy levels corresponding to the vacuum level, work function, valence band maxima and conduction band minima respectively.

5.5 Energy band diagram for hybrid Li-PRBs

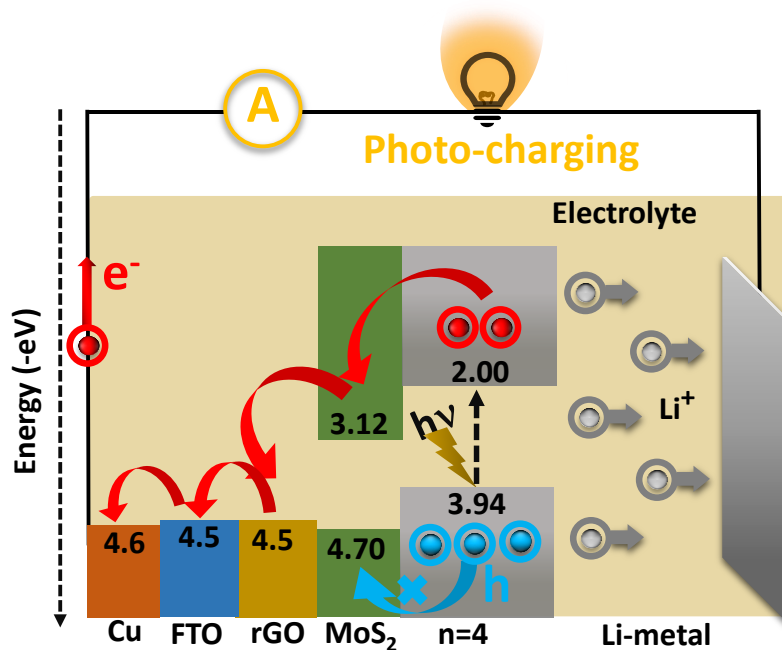


Figure 5.3 Energy band diagram showing the transport of photo generated electrons and holes in the demonstrated Li-PRB device.

The demonstrated Li-PRB uses RP perovskite as active material for solar energy absorbance and storage of Li-ions, where the efficient extraction of photo-generated electrons from RP perovskites to the current collector is achieved via favorable energy landscape formed by perovskite-MoS₂ heterojunction, ETM and electrodes. As explained in energy band diagram of proposed Li-PRB

(Figure 5.3), during OCV charging, the photons of energy larger than the band gap energy of RP perovskite ($n=4$) gets absorbed by the perovskite crystals and results in the formation of photo-generated electron-hole pairs, which gets dissociated at the interface of perovskite and MoS_2 heterojunction owing to the lower CBM of MoS_2 ($E_c \sim 3.12$ eV) [Wang et al., 2017b]. The photo-generated electrons get transported to rGO from CBM of MoS_2 due to lower work function of rGO ($\Phi \sim 4.5$ eV), which is added in the slurry as carbon additive and served as ETM for MoS_2 . Finally, these photoelectrons reach the current collector Cu ($\Phi \sim 4.6$ eV) via FTO ($\Phi \sim 4.5$ eV) to get into the external circuit of Li-PRB. The photo-generated holes do not get extracted from the RP perovskite and repels Li-ion towards the anode (Li-metal) from RP perovskite to reduce into Li.

5.6 Photo-electrochemical properties of hybrid Li-PRBs

5.6.1 CV for LIB and hybrid Li-PRBs under dark and illumination

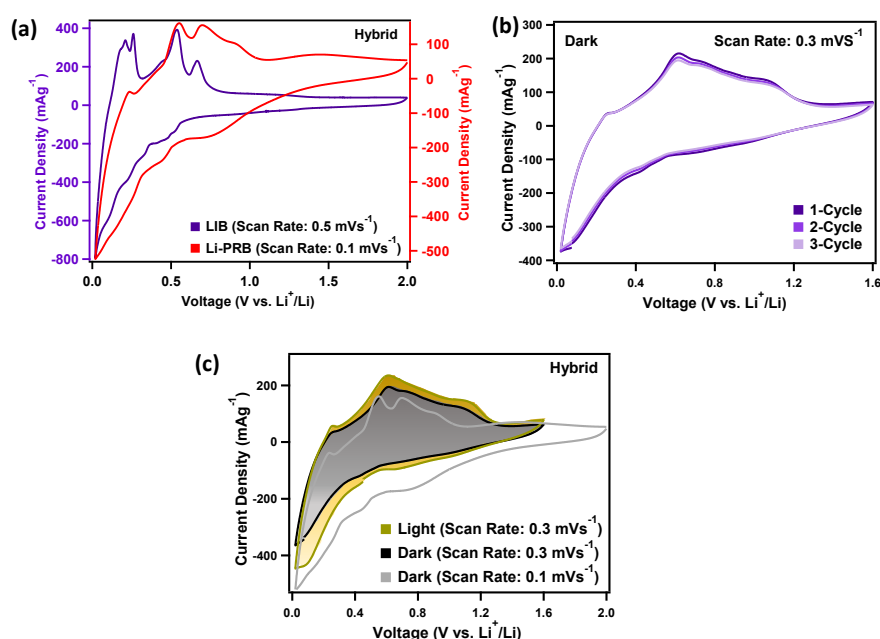
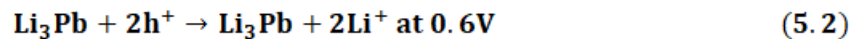
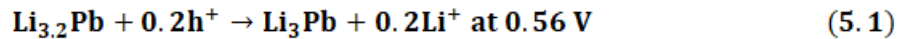


Figure 5.4 (a) CV profiles for hybrid Li-PRB at 0.5 mVs⁻¹ and 0.1 mVs⁻¹ respectively under dark condition ranging from 0.02-2.00 V. (b) CV profiles of Li-PRB at 0.3 mVs⁻¹ under dark condition ranging from 0.02-1.6 V. (c) CV profile of hybrid Li-PRB under dark and illumination conditions at a scan rate of 0.3 mV s⁻¹. CV profile of Li-PRB recorded at 0.1 mV s⁻¹ is added to show the clear redox peaks as observed in Figure (c).

As observed in **Figure 3.9e of chapter 3**, the presence of MoS_2 has increased overall absorbance while maintaining the band gap of the perovskite material, which is attributed to more light absorption due to improved surface shape and crystallinity of the perovskite films. Such increased absorbance would result in improved solar energy absorption by the hybrid electrode, resulting in the generation of a higher number of electrons and holes [Ansari et al., 2023b]. As per the results obtained from various structural, electrochemical and optical characterizations discussed above, the hybrid electrodes are found to be superior in performance compared to the pristine, therefore the hybrid electrode based Li-PRBs are interrogated further. The CV measurements of hybrid Li-PRB are performed in 0.02-2.00 V voltage window at the scan rate of 0.1 mVs⁻¹ under dark conditions which has shown the redox peaks at 0.52 / 0.69 V, 0.34 / 0.56 V and 0.14 / 0.24 V (**Figure 5.4a, Red Curve**). These redox peaks are found to be closely matching with the redox peaks observed for the corresponding conventional LIB (**Figure 5.4a, Blue Curve**), which confirms the similar operation of FTO based Li-PRB and conventional LIB. Further, the CV for Li-PRB is recorded at 0.3 mV s⁻¹ scan rate in the 0.02-1.6 V voltage window under illumination (white LED, 12.0 mWcm⁻²) which showed that the swept CV area has increased by 27.8 % compared to the CV curve recorded under dark at similar conditions (**Figure 5.2b-c**). It must be noted that the purpose of performing dark CV

profile at a scan rate of 0.1 mV s^{-1} is to resolve the redox peaks for our hybrid Li-PRB, since these peaks are not well resolved at 0.3 mV s^{-1} , as at such scan rates the FTO based Li-PRB system does not provide enough time for the completion of redox reactions as well as collection of current. The following electrochemical reactions (5.1) and (5.2) occur at photoelectrode during OCV charging:



At the counter electrode, the photo-generated electrons will reduce the Li-ions as shown in electrochemical reaction (5.3):



5.6.2 GCD profiles for hybrid Li-PRBs under dark and illumination

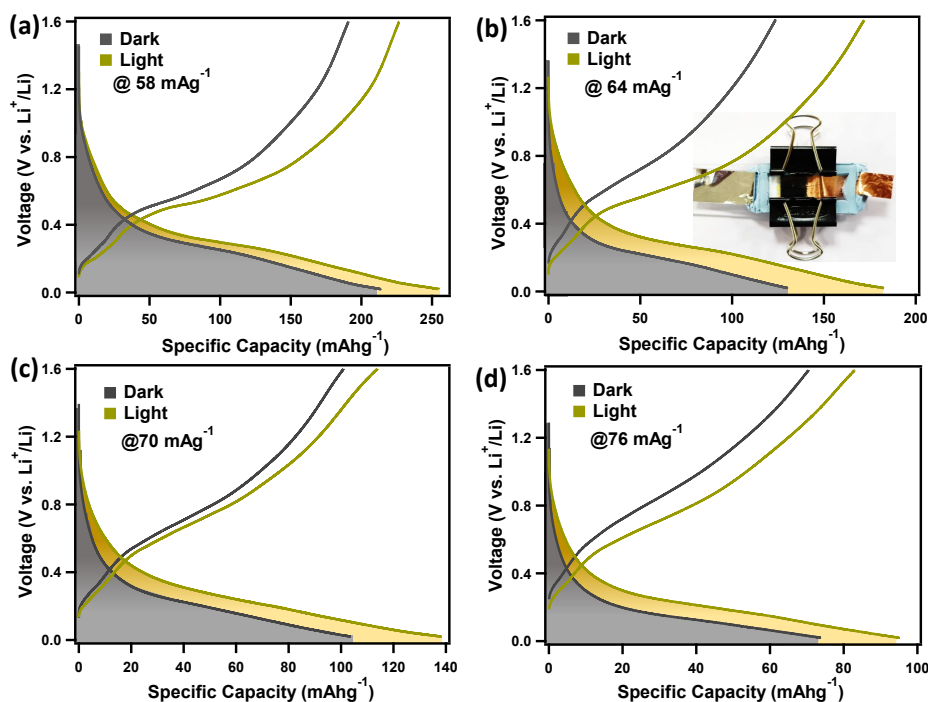


Figure 5.5 GCD profiles of Li-PRB measured under dark and illumination conditions at current densities of (a) 58 mA g^{-1} , (b) 64 mA g^{-1} (inset shows the camera image of Li-PRB), (c) 70 mA g^{-1} and (d) 76 mA g^{-1} . White LED (12.0 mWcm^{-2}) is used as illumination source.

This enhancement in the CV area, under illumination, is attributed to the generation of photo excited electrons and holes in perovskite material which enhance the redox current as a consequence of more number of sites accessible for the lithiation and delithiation. As photo-batteries are known for their photo-enhanced specific capacities, therefore the GCD measurements are performed on the Li-PRB under dark and light conditions at different current densities for 0.02 - 1.6 V voltage window. **Figure 5.5a-b** shows the GCD curves for the Li-PRB device (shown in the inset) performed under dark and light (white LED, 12.0 mWcm^{-2}) conditions at 64 mA g^{-1} and 76 mA g^{-1} current densities. As anticipated from CV, the GCD measurements revealed an increase in discharge specific capacity under illumination from 129.77 mAhg^{-1} to 180.83 mAhg^{-1} (photo-enhanced: 39.34%) and 73.79 mAhg^{-1} to 94.93 mAhg^{-1} (photo-enhanced: 28.64%) corresponding to 64 mA g^{-1} and 76 mA g^{-1} current densities respectively. Similarly, increase in discharge specific capacity under illumination is observed from 213.41 mAhg^{-1} to 254.07 mAhg^{-1} (photo-enhanced: 19.05%) and 103.66 mAhg^{-1} to 137.96 mAhg^{-1} (photo-enhanced: 33.00%) corresponding to 58 mA g^{-1} and 70 mA g^{-1} current densities respectively (**Figure 5.5c-d**). The charge and discharge curves recorded at 58 mA g^{-1} under dark and illumination has shown charging plateaus at 0.26 V and 0.54 V and discharging plateau at 0.32 V , which are found to be matching with the redox peaks in CV respectively (**Figure 5.4a**).

5.6.3 Rate cycling performance for hybrid Li-PRBs under dark and illumination

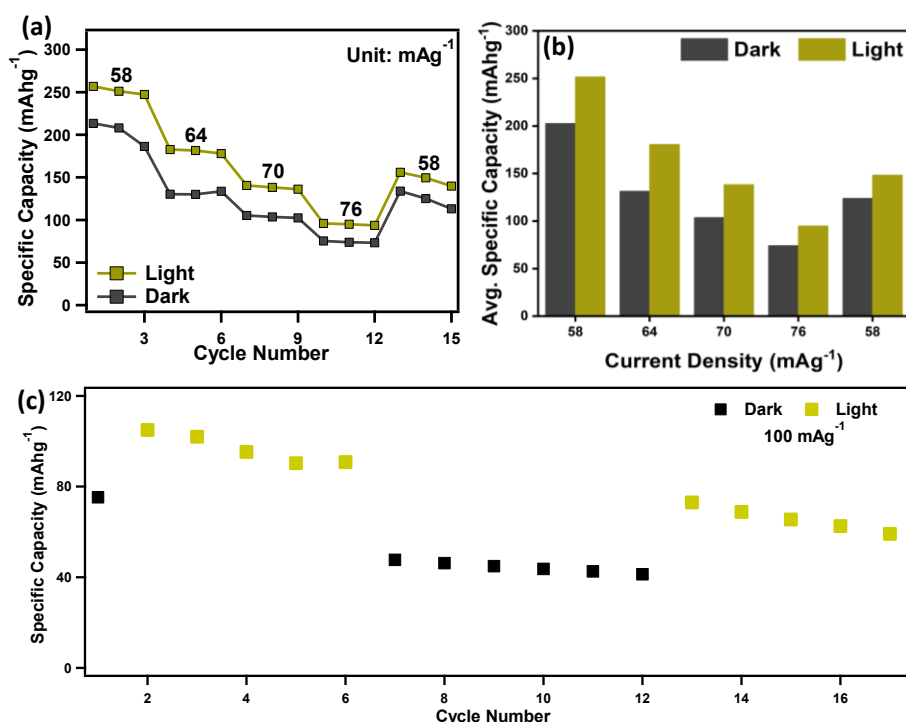


Figure 5.6 (a) Rate cyclability performance of hybrid Li-PRB recorded under dark and illumination condition at different current densities and (b) shows the corresponding enhancement in the average discharge specific capacities due to OCV charging. (c) Long cycling for hybrid Li-PRB under dark and illumination conditions at a current density of 100 mA g⁻¹. White LED (12.0 mWcm⁻²) is used as illumination source.

Further, the rate cyclability are investigated for the same Li-PRB device at various specific current densities ranging from 58 to 76 mA g⁻¹ by performing three GCD cycles under dark and light condition at each current density (**Figure 5.6a**). Here, Li-PRB demonstrated average discharge specific capacity of 202.61 mA h g⁻¹ (capacity retention: 87.31 %) for 1-3 cycles performed at current density of 58 mA g⁻¹ under dark condition which increased to 251.75 mA h g⁻¹ (capacity retention: 96.23 %; photo-enhanced: 24.25 %) under illumination condition (**Figure 5.6a-b**). As the current density increased, the average discharge specific capacities under illumination is enhanced from 128.66 mA h g⁻¹ (capacity retention: 96.56 %) to 180.67 mA h g⁻¹ (capacity retention: 97.39 %; photo-enhanced: 40.42 %) for 4-6 cycles performed at 64 mA g⁻¹, from 103.76 mA h g⁻¹ (capacity retention: 97.13 %) to 138.27 mA h g⁻¹ (capacity retention: 96.82 %; photo-enhanced: 33.27 %) for 7-9 cycles performed at 70 mA g⁻¹ and from 74.15 mA h g⁻¹ (capacity retention: 97.21 %) to 94.82 mA h g⁻¹ (capacity retention: 97.51 %; photo-enhanced: 27.86 %) for 10-12 cycles performed at 76 mA g⁻¹ (**Figure 5.6a-b**). After exposure to high current densities, when the current density is reduced back to 58 mA g⁻¹ the average discharge specific capacity recovered to 123.97 mA h g⁻¹ under dark condition (capacity retention: 84.49 %, for 13-15 cycles) which further enhanced to 148.39 mA h g⁻¹ under light (capacity retention: 89.59 %; photo-enhanced: 19.70 %) (**Figure 5.6a-b**). Compared to the first reported RP perovskite (n=1) based Li-PRB, these RP perovskite (n=4)-MoS₂ hybrid photoelectrodes-based Li-PRB has shown improved performance and good stability when operated under different current densities [Ahmad et al., 2018].

To further investigate the stability of our hybrid Li-PRB, I recorded the GCD cycling under the dark and illumination at a high current rate of 100 mA g⁻¹ in a voltage range of 1.6-0.5 V (**Figure 5.6c**). Compared to the dark conditions the specific capacity was found to be increased from 75.3 to 105 mA h g⁻¹ for the initial cycles and even after 12 cycles the capacity of the PRB increased from 41.3 to 73 mA h g⁻¹ under illumination. The enhancement in the specific capacity even after these number of cycles suggests that PRB is still responsive to light and demonstrates the stable performance over long cycles under high current rates.

5.7 Temperature dependent study for hybrid Li-PRBs

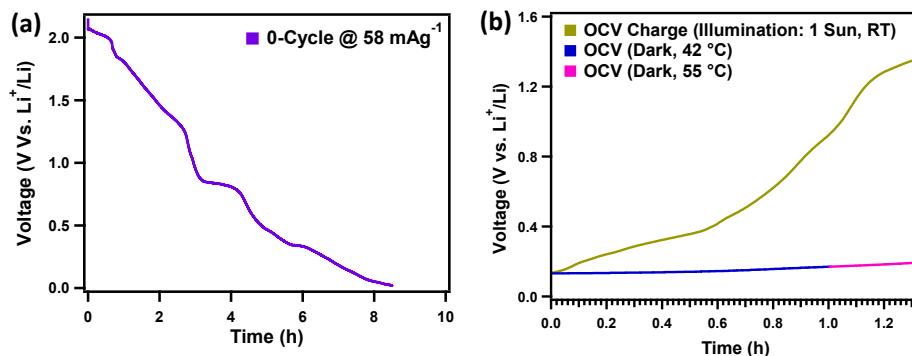


Figure 5.7 (a) 0th cycle discharge profile of Li-PRB under dark condition at a current density of 58 mA g⁻¹. (b) Temperature dependent OCV- profiles of hybrid Li-PRB. OCV profile under 1 Sun illumination is added for comparison.

In order to investigate the effect of temperature on OCV, freshly prepared hybrid PRB is placed on the stage equipped with heater, at room temperature hybrid Li-PRB is first discharged to 0.02 V galvanostatically at a discharge current density of 58 mA g⁻¹ under dark conditions and kept for rest (1 hour) to stabilize OCV (**Figure 5.7a**). Next, OCV (without introducing external current) is recorded under dark conditions for ~1.0 hour at 42 °C (**blue curve**), where OCV has shown slight rise from 0.13 V to 0.17 V ($\Delta V=0.04$) (**Figure 5.7b**). The temperature of the stage is further raised to 55 °C (**pink curve**) and OCV is recorded for next ~0.32 hour, where OCV has shown rise from 0.17 V to 0.19 V ($\Delta V=0.02$). Temperature of 55 °C is chosen considering the operational temperature of the devices in territorial conditions. Thus, under temperature treatment (upto 55 °C) for more than 1.0 hour, the total rise in OCV of Li-PRB is very small ~0.06 V, which is insignificant compared to the observed photocharging characteristics. To confirm this further, when the hybrid Li-PRBs is operated under 1 Sun illumination at room temperature, the OCV has shown rapid rise from 0.13 V to 1.35 V ($\Delta V=1.22$) (**yellow curve**) for ~1.32 hours. Such temperature dependent OCV measurements confirmed that, unlike solar illumination, heating does not influence the change in OCV significantly and therefore does not have much contribution in the specific capacity. Our experiments provide prelim insights about the role of external temperature, and more sophisticated experiments can be planned to probe the local temperature rise of the PRB.

5.8 In-Situ and OCV measurements for hybrid Li-PRBs

To understand how light can solely enhance the specific capacity of the Li-PRB, I performed an in-situ measurement, where a freshly fabricated Li-PRB is first discharged to 0.02 V and then kept without any load. In 6 minutes, the rise in OCV (without introducing external currents) is saturated to 0.06 V (**red curve, Figure 5.8a, inset**). Next, the white light LED is turned ON and the voltage of Li-PRB has increased from 0.06 V to 0.47 V in 11.14 hours (**yellow curve, Figure 5.8a**). The Li-PRB is then galvanostatically discharged at 40 mA g⁻¹ under illumination and it is observed that the OCV of Li-PRB has dropped gradually from 0.47 to 0.30 V (**magenta curve, Figure 5.8a**) in 8.56 hours. Afterwards, the light is turned-OFF and the OCV of Li-PRB dropped sharply from 0.30 to 0.02 V (**black curve, Figure 5.8a**) in 4.12 hours, as expected from the dark discharge response. These results reveal that the discharged time of Li-PRB under illumination is twice than the discharge time under dark condition, which highlights the role of photo-generated charge carriers discussed above. It must be noted that during simultaneous OCV charge and galvanostatic discharge process the voltage drop is ~1.6 times less compared to the just galvanostatic discharge under dark conditions. This is because of OCV charge and galvanostatic discharge occur concurrently in Li-PRBs. Thus, under controlled load conditions the OCV charge and discharge current rates can be balanced to obtain a constant power output which can be useful for continuous operation of various electronic devices such as IoT sensors etc. The PC-SE is estimated by first discharging a freshly assembled hybrid Li-PRB from its OCV (~2.78 V) to 0.02 V galvanostatically.

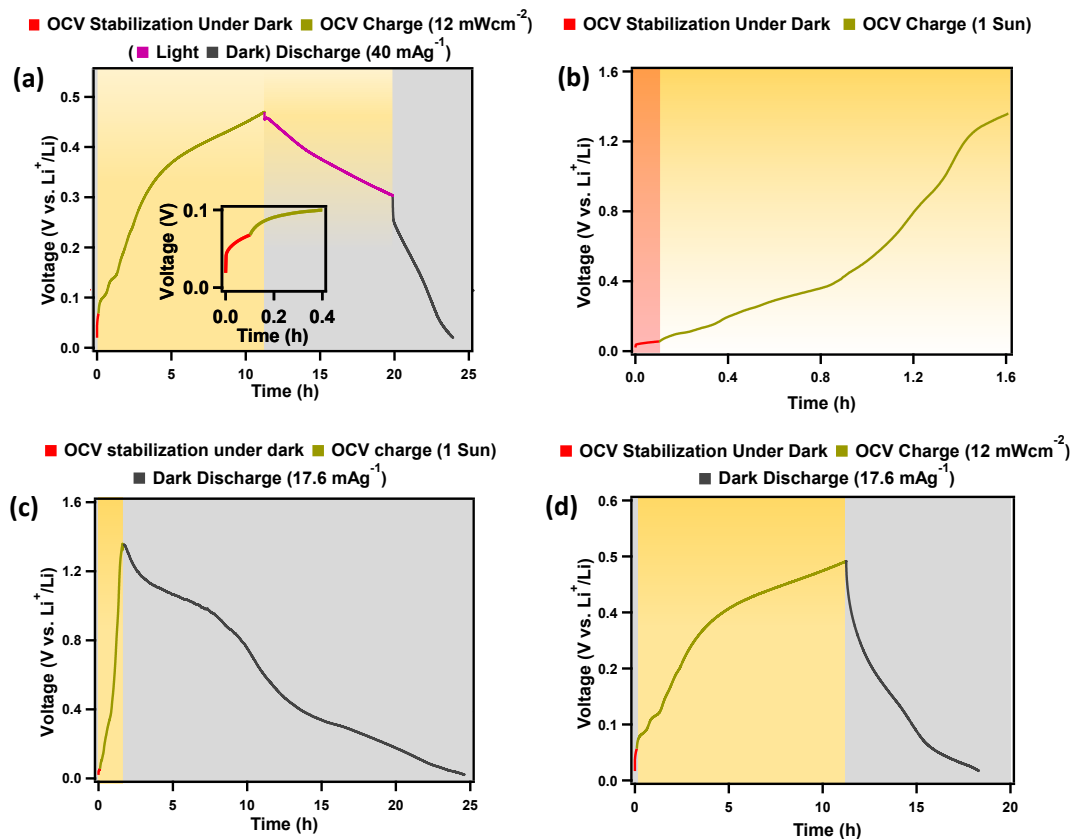


Figure 5.8 (a) OCV charging monitoring of Li-PRB under illumination (without external current, yellow curve), in-situ galvanostatic light discharge (magenta curve) and dark discharge (black curve) at current density of 40 mA g^{-1} . Inset plot shows the saturation of OCV under dark condition. (b-c) OCV charging of Li-PRB under 1 Sun illumination (Xe-lamp, 100 mW cm^{-2}) from 0.05 V to 1.35 V after OCV stabilization followed by galvanostatic dark discharge at current density of 17.6 mA g^{-1} . (d) OCV charging of Li-PRB under white LED illumination for 11.14 hours followed by discharge at specific currents of 17.6 mA g^{-1} under dark condition (black curve). The red curves in figure (a-d) show the OCV stabilization after self-charging.

Afterwards, the PRB is kept at rest for ~6 minutes in dark condition to stabilize the rise in OCV from 0.02-0.05 V (**red curve, Figure 5.8b**). Next, OCV charging is initiated using standard 1 Sun illumination light source (Xe-lamp, 100 mW cm^{-2}). As soon as the illumination is turned ON the OCV shows a sudden rise and has increased from 0.05 to 1.35 V in ~1.63 hours (**yellow curve, Figure 5.8b**). After the OCV value is saturated (**Figure 5.8c**), the light is turned OFF and PRB is galvanostatically discharged to 0.02 V at a steady current density of 17.6 mA g^{-1} in dark, which took ~22.85 hours. Based on the potential window, OCV charge and discharge time, incident power density, discharge current density the Li-PRBs have shown the PC-SE of 0.52 %, which is around ~16 times more compared to our previously reported 2D perovskite-based Li-PRB (**see Sub-Section 2.14.3 of Chapter 2 for details of PC-SE calculation**). Furthermore, for white LED illumination ($P_{\text{in}} \approx 12 \text{ mW cm}^{-2}$), during charging the OCV increased from 0.05 to 0.47 V in ~11.14 hours, and discharge under similar conditions took ~6.99 hours which corresponds to PC-SE of 0.043% (**Figure 5.8d**).

5.9 Spectral intensity distribution comparison between Xe-Lamp (Standard 1 Sun) and white LED

Higher PC-SE obtained using Xe-lamp is attributed to the generation of large number of electrons and holes due to broad spectral illumination compared to white LED (**Figure 5.9**). In comparison to other MHP based PRBs, the PC-SE of these RP perovskite-MoS₂ Li-PRBs is found to be highest and showed excellent capacity retention as well as specific capacity recovery in rate cyclability test under different current rates for hybrid Li-PRBs (**see Table 5.1**).

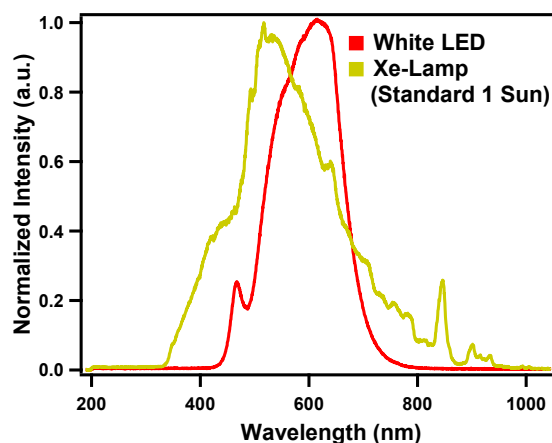


Figure 5.9 Normalized spectral intensity distribution for Xe-Lamp (Standard 1 Sun) and white LED.

5.10 Ex-Situ measurements for hybrid Li-PRBs

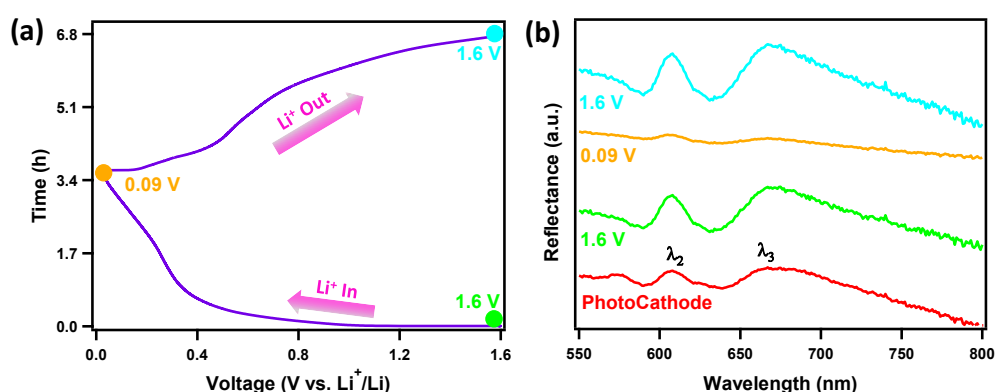


Figure 5.10 (a) Initial galvanostatic discharge-charge curve of Li-PRB as a function of state of charge and (b) shows the ex-situ reflection spectrums of hybrid photoelectrode measured at corresponding different state of charge.

As per the crystal structure schematic shown in **figure 3.1a** of **Chapter 3**, the RP perovskite material forms layered structures with alternate arrangements of inorganic layers composed of $(\text{PbI}_6)^{4-}$ inorganic octahedrons separated by organic spacer cations (BA). The mismatch in the energy band gaps of both inorganic layers ($\sim 2-3$ eV, well) and organic moieties (>5 eV, barrier) results in quantum confinement effect. Thus, these 2D metal halide perovskite crystal structures resemble the natural multiple quantum well (MQW) structures. Similarly, the high dielectric constant of inorganic layers and low dielectric constant of organic spacers leads to dielectric confinement effect.

Therefore, these quantum and dielectric confinement effects results in the formation of high binding energy Wannier-Mott type excitons (B.E ~ 10 meV) [Ansari et al., 2023b], which are confined within the inorganic nanosheets. Such large binding energy of 2D metal halide perovskites enables their visibility at room-temperature (300 K). Since, these confinement effects are highly dependent on the elemental compositions as well as structural variations of the 2D MHP, thus we have investigated these room-temperature excitons to better understand the photocharging mechanism in hybrid photoelectrodes by observing the ex-situ reflection spectra of the photoelectrode as a function SoC (**Figure 5.10a**). The reflectance spectra of photoelectrode, recorded before assembling into PRB (**red curve, Figure 5.10b**), has shown two prominent exciton reflection peaks at 607 nm (λ_2) and 666 nm (λ_3). The PRB discharged at 1.60 V (**green dot, Figure 5.10a and green curve, Figure 5.10b**) has shown similar exciton reflection peaks, which shows that at 1.6 V the optical properties of RP perovskite remain intact. However, as Li-PRB is discharged galvanostatically (58 mA g^{-1}) to 0.09 V (**yellow dot, Figure 5.10a**), the intensity of these exciton reflectance peaks reduced significantly

(yellow curve, Figure 5.10b), without any shift in their peak positions, due to increase in photon scattering caused by lithiated perovskite crystals which affects the interaction of light with perovskite [Merryweather et al., 2021]. Thus the reduction in reflection peak intensity confirms partial lithiation of RP perovskite crystals. Additionally, the lithiation of perovskite crystal also reduces the dielectric confinement effect, which in turn reduces the exciton reflection peak intensity. When the Li-PRB is galvanostatically (58 mA g^{-1}) charged from 0.09 V to 1.6 V (sky blue dot, Figure 5.10a), the intensity of reflectance peaks is enhanced back to actual, which confirms the delithiation of RP perovskite crystals (sky blue curve, Figure 5.10b). These ex-situ reflection measurements confirmed that hereditary of RP perovskite material recovers in one complete cycle [Boruah et al., 2021b].

5.11 Photo-battery module

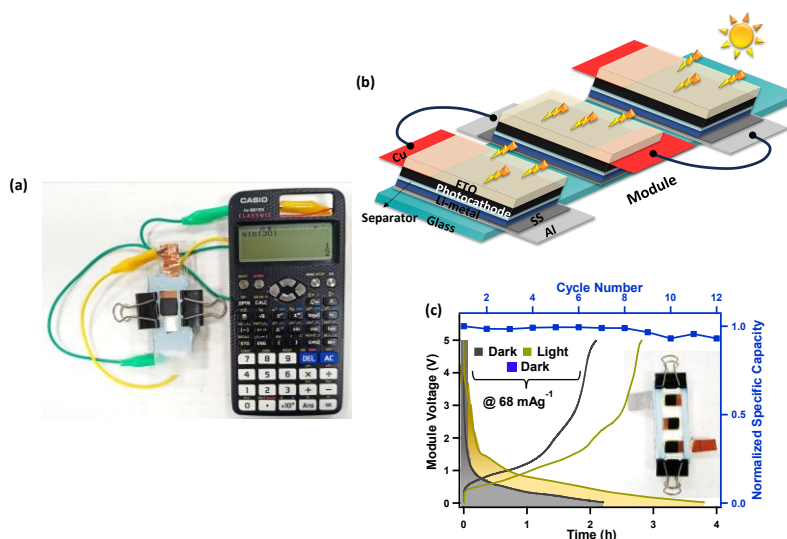


Figure 5.11 (a) Demonstration showing hybrid Li-PRB powering scientific calculator. (b) Schematic diagram of the fabricated photo-battery module comprising of three Li-PRB cells connected in series. (c) GCD under dark and illumination for photo-battery module with three cells connected in series (left vs bottom axis). Normalized dark discharge specific capacity of photo-battery module (right vs top axis). Inset shows camera image of the module. White LED (12.0 mW cm^{-2}) is used as illumination source.

Finally, the real-life application of the developed Li-PRB is demonstrated by powering a scientific calculator after removing the battery and solar panel from the calculator (**Figure 5.11a**), where the photo-battery was able to power the calculator for more than 7 days continuously. Further, to enhance the overall operational voltage window, we fabricated a photo-battery module (**Schematic showed in Figure 5.11b**) by connecting three Li-PRBs in series (**Figure 5.11c, Inset**). Under dark conditions, the Li-PRB module discharged from 5.00 V to 0.02 V in 2.2 hours at a current density of 68 mA g^{-1} , which increased to 3.81 hours when the module is discharged galvanostatically under illumination (**left vs. bottom axis, Figure 5.11c**). Similar characteristics are observed when the module is charged galvanostatically under dark and illumination. The stable operation of Li-PRB module is demonstrated by measuring more than 10 GCD cycles under dark condition which showed nearly steady discharge specific capacity (retention: 93 %) (**right vs. top axis, Figure 5.11c**).

Table 5.1 Comparison of photoelectrochemical performance of demonstrated (BA)₂(MA)₃Pb₄I₁₃-MoS₂ hybrid Li-PRB with other reported 2D and 3D perovskites-based energy storage devices.

Electrode and Device Type	Counter Electrode	Electrolyte	1 st Cycle Capacity (mAhg ⁻¹) Under Dark Condition	Specific Capacity (mAhg ⁻¹) and Capacity Retention (%) after n th cycle Under Dark Condition	Current Density (mA g ⁻¹)	Voltage Window (V)	PC-SE (η %) Under Xe-Lamp (P _{in} ~100 mWcm ⁻²)	Ref.
(CH) ₂ PbI ₄ : PCBM/rGO: PVDF (80:10:10) on FTO; Li-PRB	Li-metal	1 M LiPF ₆ , EC:DEC (1:1 v/v)	-	-	-	-	0.034 % with FTO as current collector for 2.0-2.95 voltage window	[Ahmad et al., 2018]
Cs ₂ BiI ₉ : PCBM: PVDF (80:10:10) on FTO; Li-PRB	Li-metal	1 M LiPF ₆ in EC:DMC (1:1 v/v)	~155	~58 and ~38 % after 3 cycles	50	0.0-2.5	0.071 % and 0.43% with FTO and Carbon Felt as current collector respectively for 0.9-2.3 voltage window	[Tewari et al., 2021]
DAPbI: CNT: PVDF (60:30:10) ; Li-PRB	Li-metal	1 M LiTFSI DOL:DME (1:1 v/v)	-	-	-	-	0.49% for 1.97-2.17 voltage window	[Chen et al., 2022a]
(BA) ₂ (MA) ₃ Pb ₄ I ₁₃ :MoS ₂ : rGO: Super P, PVDF (84.6:0.4:5:3:7) on FTO; Li-PRB	Li-metal	1 M LiPF ₆ in EC:DMC (1:1 v/v)	~213	~186 and ~88 % after 3 cycle	58	0.02-1.6	0.52% for 0.05-1.35 voltage window	This Chapter

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