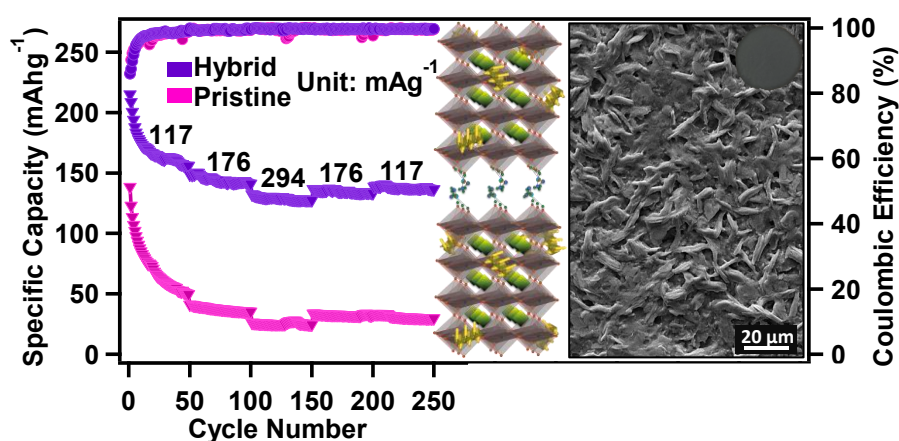


Ruddlesden-Popper 2D Perovskite-MoS₂ Hybrid Heterojunctions based Anodes for Efficient Li-Ion Batteries

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LIBs are the dominant power source in portable electronics, have made advances into the electric car sector, and have the potential to enter the utility market for grid-energy storage. Depending on the application, decisions between many performance parameters such as energy, cycle life, cost, and safety are typically required, which are accompanied by significant materials chemistry challenges. In this chapter, I have mentioned the electrochemical performance of RP perovskite (BA)₂(MA)₃Pb₄I₁₃ (n=4) and MoS₂ nanoflakes heterojunction-based material. Hybrid LIBs have demonstrated an average discharge specific capacity of 144.46 mAhg⁻¹ (capacity retention: 94.95 %) and 129.17 mAhg⁻¹ (capacity retention: 96.36 %) for 50 cycles when operated at 176 mAg⁻¹ and 294 mAg⁻¹ respectively compared to the pristine LIBs which have shown specific capacity of 37.48 mAhg⁻¹ and 25.60 mAhg⁻¹ under similar conditions.

4.1 Different MHP based energy storage devices

In recent years, MHPs: (can be three dimensional; 3D or two dimensional; 2D) have shown a significant amount of attention worldwide from the scientific community for the fabrication of optoelectronic devices including photovoltaics, light emitting diodes, photodetectors, photocatalytic hydrogen generation, and sensors due to their excellent photophysical properties. Moreover, these MHP involves in the development of LIBs due to their ability to store the Li-ion. Where the energy storage mechanism involves intercalation, conversion as well as alloying reactions. In 2015, Xia et al. first time used MAPbX_3 ($\text{X}=\text{Br/I}$) to develop LIB, where MAPbI_3 and MAPbBr_3 has shown first discharge specific capacities of 43.6 mAhg^{-1} and 331.8 mAhg^{-1} respectively at a current density of 200 mA g^{-1} . The specific capacity of MAPbBr_3 based LIB is six times higher than the maximum theoretical specific capacity (55.96 mAhg^{-1}). Furthermore, its specific capacity is roughly equivalent to commercially available graphite, implying large potential volumetric energy density growth. In 2018, Daniel et. al has published a LIB using RP perovskite of type $(\text{PA})_2(\text{MA})_2\text{Pb}_3\text{Br}_{10}$ and shown specific capacity of $\sim 175 \text{ mAhg}^{-1}$ at a current density of 425 mA g^{-1} after first discharge which further reduced to $\sim 35 \text{ mAhg}^{-1}$ after 10^{th} cycles [Ramirez et al., 2018]. Subsequently, in 2022 Chen et. al published a LIBs using DAPbI perovskite as active material [Chen et al., 2022a]. After enclosing the LIB in a glass bottle, they reported a specific capacity of $\sim 78 \text{ mAhg}^{-1}$ at a current density of 20 mA g^{-1} which further reduced to $\sim 21 \text{ mAhg}^{-1}$ after 20^{th} cycles. Recently (2023), Shu-Chi-Wu et. al fabricated aluminum ion battery using $(\text{iBA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ RP perovskite and reported $\sim 275 \text{ mAhg}^{-1}$ specific capacity for the first discharge cycle after SEI layer formation at a current density of 200 mA g^{-1} , which further reduced to $\sim 173 \text{ mAhg}^{-1}$ after 50^{th} cycles [Wu et al., 2023b]. Agus et. al. in 2021 has published an article related to LIB where, $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ ($n=1-4$) is used an active material. Here they demonstrated that the specific capacity of the RP perovskites depends on the number of inorganic octahedra layers. i.e., higher n-value ($n=4$) based RP perovskite has shown higher specific capacity as compared to lower n-value ($n=1$) based RP perovskites. Moreover, they reported such rise in specific capacity with n-value exhibited no role of organic spacer cation in the lithiation/delithiation process. These reports demonstrated that MHPs suffers faster specific capacity fading challenges due to the dissolution of active material at the electrode-electrolyte interface, which are the major drawbacks in the commercialization point of view [Mathieson et al., 2021a].

This issues is related to the structural and morphological properties of the MHPs, which may be improved by exploring various strategies such as use of (i) advanced fabrication, (ii) quasi-dimensional MHPs, (iii) solid state or gel electrolytes, (iv) ligand engineering of MHPs, (v) nanocomposite of MHP and inorganic nanomaterials etc [Cho et al., 2021]. Among these, for LIB 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 shown in chapter 3, $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ ($n=4$) and MoS_2 BHJ based hybrid material has shown remarkable improvement in the structural and morphological properties of the RP perovskite using thin film as compared to pristine counterpart [Ansari et al., 2023a]. Such improved photo-stability and optoelectronic properties offered by the RP perovskite- MoS_2 hybrids make them a potential system worth exploring for the LIBs.

4.2 Structural properties using gaussian fitting

The RP perovskite ($n=4$)+ MoS_2 is schematically represented in **figure 4.1a** where the crystal structure of RP perovskite $n=4$ shows the four inorganic octahedron $[\text{PbI}_6]^{4-}$ layers and the MoS_2 flakes forming the heterostructure configuration of type (II) [Fang et al., 2019; Xia et al., 2022; Zhao et al., 2020; Zhou et al., 2022]. Thin film XRD measurements are performed on $n=4$ and $n=4+\text{MoS}_2$ samples which are shown in **Sub-Section 3.4.1 of Chapter 3**. The thin film XRD measurements confirmed the orthorhombic crystal structure and RP phase of the pristine perovskite material with two intense diffraction peaks at $2\theta=14.2^\circ$ and $2\theta=28.5^\circ$ [Cao et al., 2015].

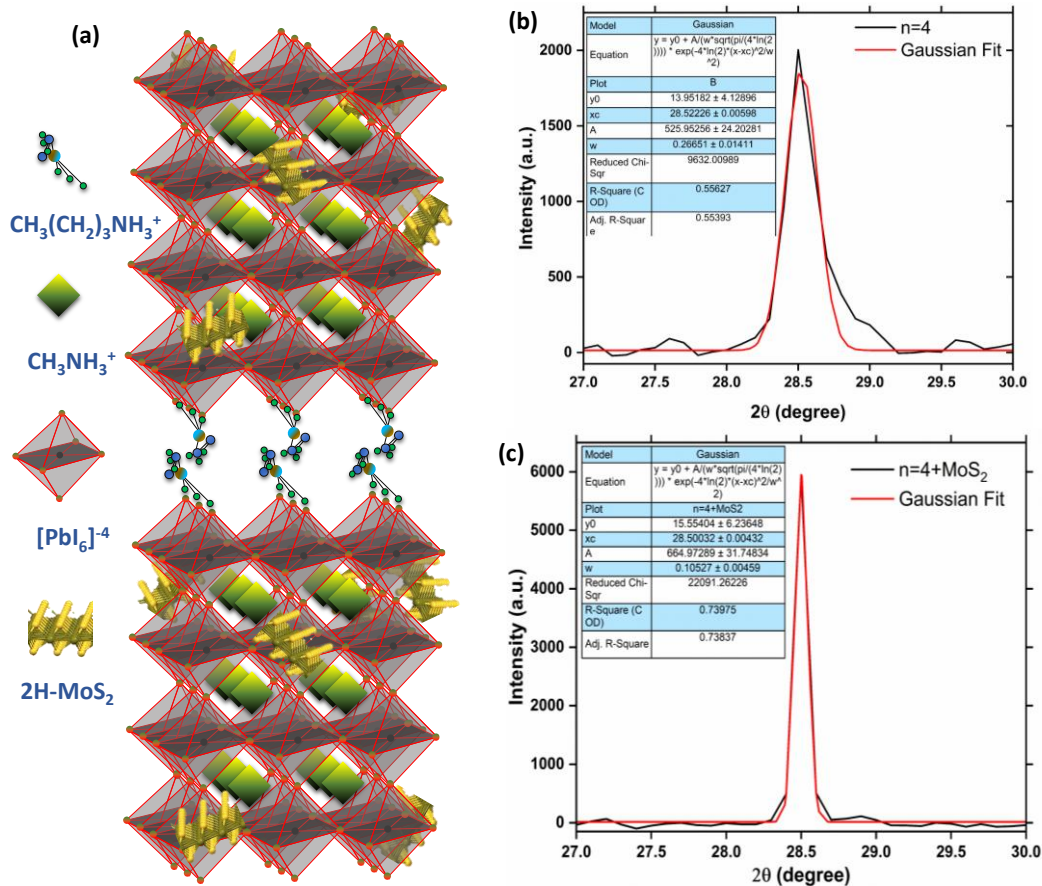


Figure 4.1 (a) Schematic illustration of crystal structure for the RP perovskite ($n=4$) and MoS_2 hybrid $((\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13} + \text{MoS}_2)$ showing the formed heterostructures. Gaussian fitting of the diffraction peak at $2\theta=28.5^\circ$ for (b) pristine ($n=4$) RP perovskite and (c) RP perovskite ($n=4$)+ MoS_2 .

Here I have shown the gaussian fitting for the XRD peak at $2\theta=28.5^\circ$ and found that pristine RP perovskite ($n=4$) thin film has shown larger FWHM ($\sim 0.27^\circ$, **Figure 4.1b**), whereas RP perovskite ($n=4$)+ MoS_2 thin film has shown smaller FWHM ($\sim 0.11^\circ$, **Figure 4.1c**), which provide insights about the improvements in the film packing due to heterogeneous nucleation in case of RP perovskite ($n=4$)+ MoS_2 .

4.3 Morphological properties

4.3.1 Top view surface morphology for $n=4$ and $n=4+\text{MoS}_2$ dropcasted films

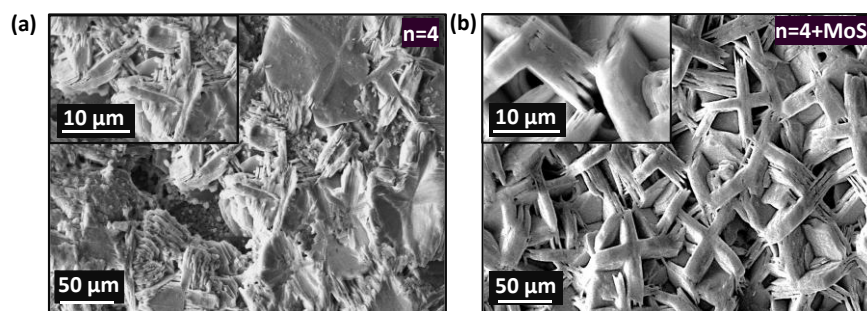


Figure 4.2 Top view of SEM image of (a) $n=4$ and (b) $n=4 + \text{MoS}_2$ dropcasted film. Inset image shows the close-up view.

When hybrid solutions are casted, during crystallization the perovskite crystals undergoes heterogeneous nucleation triggered by the presence of MoS₂ heterogeneous phase in the perovskite precursor solution [Liu et al., 2020]. Such heterogeneous nucleation of perovskite crystals is known to improve the surface morphology and packing of film, which is confirmed by the top view SEM images performed on drop-casted films of pristine RP perovskite (n=4) and n=4+MoS₂. As compared to the pristine (**Figure 4.2a**), the MoS₂ doped RP perovskite film has formed vertically aligned stacks of perovskite crystals giving an interconnected network with improved morphology (**Figure 4.2b**).

4.3.2 Cross-sectional view surface morphology for n=4 and n=4+MoS₂ dropcasted films

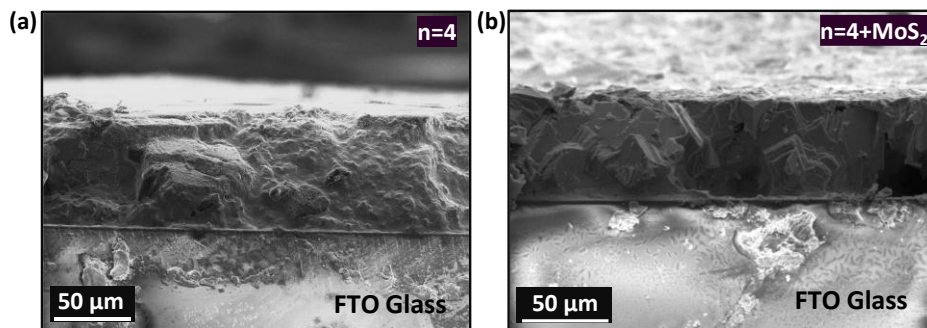


Figure 4.3 Cross-section FESEM images for (a) n=4 and (b) n=4 + MoS₂ dropcasted films.

To investigate it further, I have performed the cross-section FESEM imaging for drop-casted n=4 and n=4 + MoS₂ films. Where n=4 + MoS₂ film has shown presence of vertically oriented perovskite crystals with an average size of ~65 μm, which is in close agreement to what is observed for the top view drop-casted SEM images. Whereas the pristine perovskite film has not shown the presence of such vertically oriented crystals. Thus, these cross-section FESEM images reveal improved surface morphology, crystal packing as well as formation of good interface with FTO substrate for the MoS₂ doped RP perovskite films (**Figure 4.3a-b**), compared to pristine perovskite samples. Such vertically aligned layered perovskite crystals arrangement is ideal for the battery electrodes as they offer least resistive path to the Li-ions during intercalation and de-intercalation process [Mathieson et al., 2021b]. Moreover, such surface morphology of the hybrid electrodes improved the perovskite crystals as well as reduces defects, charge transfer resistance and trap-assisted recombination [Liu et al., 2020]. It is also noted that top and cross-sectional view of MoS₂ doped drop-casted films of perovskite sample don't show any presence of MoS₂ nanoflakes due to their small quantity (~0.4 wt %) rather than improving the surface morphology and film compactness as compared to pristine sample (n=4). This provides insights about the role of MoS₂ nanoflakes in improving the structural properties of RP perovskites.

4.3.3 Top view surface morphology for hybrid electrode

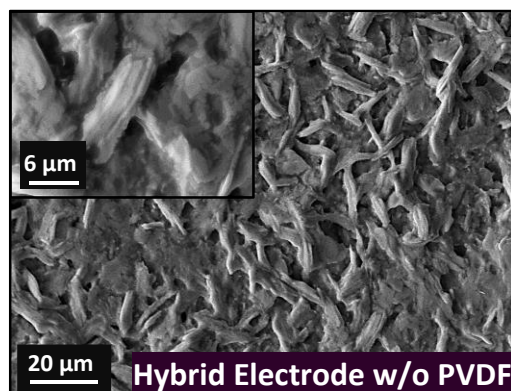


Figure 4.4 Top view of SEM image of dropcasted hybrid electrode without PVDF. The inset shows the close view.

Top view SEM image for hybrid electrode without PVDF is shown in **figure 4.4**. Where carbon additive such as rGO super-P are uniformly distributed over the surface. These additives will help to improve the conductivity of the film, when PVDF is added.

4.4 Composition of pristine and hybrid electrodes for LIB

Pristine electrode contains RP perovskite (85 wt %), whereas hybrid electrode includes RP perovskite (84.6 wt %) and MoS₂ nanoflakes (0.4 wt %). For both electrodes super-P (3 wt%) and rGO (5 wt %) served as carbon additives and PVDF (7 wt %) is used as a binder. 20 μ l (1.7 mg of perovskite) slurry is casted on Cu-disc current collector and dried at 70 °C inside glove box for whole night to remove NMP solvent. The fabrication process for LIBs are detailed in the Sub-Section 2.13.4-2.13.5 of chapter 2.

4.5 Electrochemical Properties

4.5.1 CV for pristine and hybrid LIBs

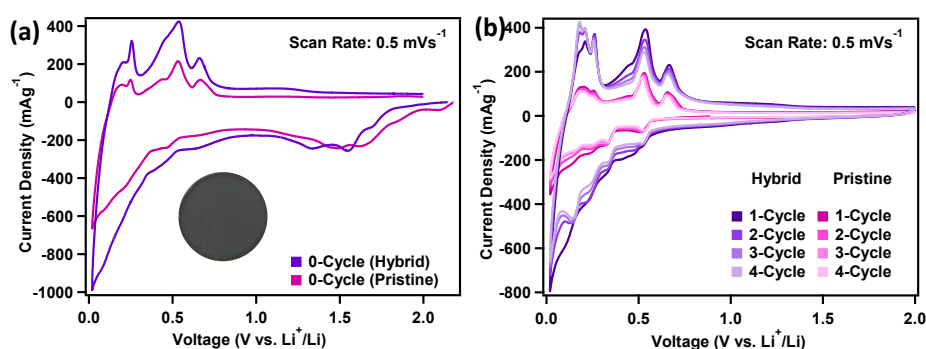


Figure 4.5 CV profiles of hybrid and pristine LIBs for (a) 0th cycle, and (b) 1 to 4-Cycle recorded at scan rate of 0.5 mV s⁻¹.

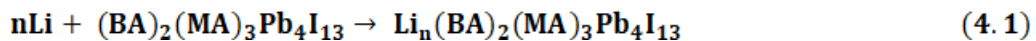
To understand the electrochemical properties of the pristine perovskite and perovskite-MoS₂ hybrid materials the CV measurements of their corresponding LIBs are performed at the scan rate of 0.5 mVs⁻¹ for 0.02-2.0 V (vs Li/Li⁺) voltage window. The 0th cycle of pristine perovskite LIB, started at the OCV ~ 2.15 V, has shown a reduction peaks around 1.47 V, corresponding to irreversible conversion of Pb(II) $\rightarrow$ Pb(0) (**Figure 4.5a, Magenta Curve**), which is attributed to the partial dissolution of [PbI₄]⁻⁴ octahedrons in liquid electrolytic medium [Tewari et al., 2022]. In hybrid LIBs, these reduction peaks shift to lower voltages (**Figure 4.5a, Blue Curve**), which is attributed to the formation of bulk heterojunction of type-II between RP perovskite and few layers of MoS₂, leading to improved charge transport across perovskite electrode [Ansari et al., 2023a].

The reduction peak around 0.67 V corresponds to the solid electrolyte interphase (SEI) formation [Tathavadekar et al., 2017]. As reported elsewhere, the reduction-oxidation processes for metal halide perovskite based LIBs involve the intercalation, conversion and alloying-dealloying reactions resulting in the formation of Li_xPb intermetallic compound of varying composition, as shown in chemical reaction equations 4.1 to 4.6 [Ahmad et al., 2014a; Dawson et al., 2017; Martos et al., 2003; Tathavadekar et al., 2017; Wood et al., 2014, 2016]. Although during reduction scan for 0th cycle of both LIBs, the peaks corresponding to alloying are not strong i.e. showing weak reduction activity, but the peaks for dealloying are strong during the oxidation cycle (**Figure 4.5a**). As observed in the subsequent cycles (1-4th cycle) for both pristine and hybrid LIBs, the CV curves has shown two redox (reduction/oxidation) peaks at 0.50 V / 0.67 V and 0.32 V / 0.52 V which are corresponding to the reversible alloying-dealloying reactions of RP perovskite (**Figure 4.5b**). The last redox peak observed at 0.14 V / 0.26 V is related to the conducting additive rGO [Xia et al., 2015]. It is noted that perovskite-MoS₂ hybrid LIB has shown very stable CV cycles, enhanced redox peak strength and swept area compared to its pristine counterpart. Moreover, the CV measurements performed for

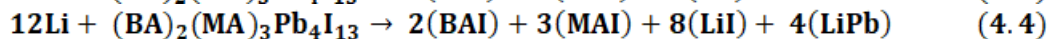
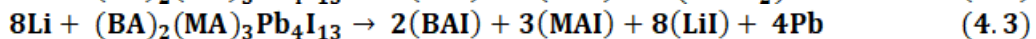
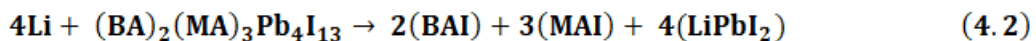
hybrid LIB (**Figure 4.5b**) does not show any electrochemical signature of the MoS₂ redox peaks which usually occurs at 1.33/1.88 V and 2.03/2.26 V [Wang et al., 2018]. Since with such a small quantity ~0.4 wt % of MoS₂ nanoflakes, it is not possible to get any contribution from MoS₂ in the overall specific capacity of the hybrid LIBs. The purpose of MoS₂ nanoflakes is to improve the structural properties (crystallinity and morphology) of RP perovskite material, which can in-turn improve the electrochemical properties of the LIBs and as demonstrated in the coming sections.

Chemical equations 4.1-4.6 showing the Intercalation, Conversion and Alloying-Dealloying reactions mechanism in RP perovskites. These reactions mechanism are adopted from ours and other previously published results [Ahmad et al., 2018; Mathieson et al., 2021b; Wood et al., 2016].

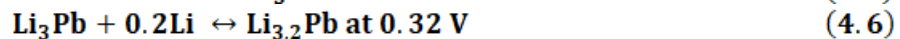
Intercalation reaction:



Conversion reaction:



Alloying-Dealloying reaction:



4.5.2 GCD for pristine and hybrid LIBs

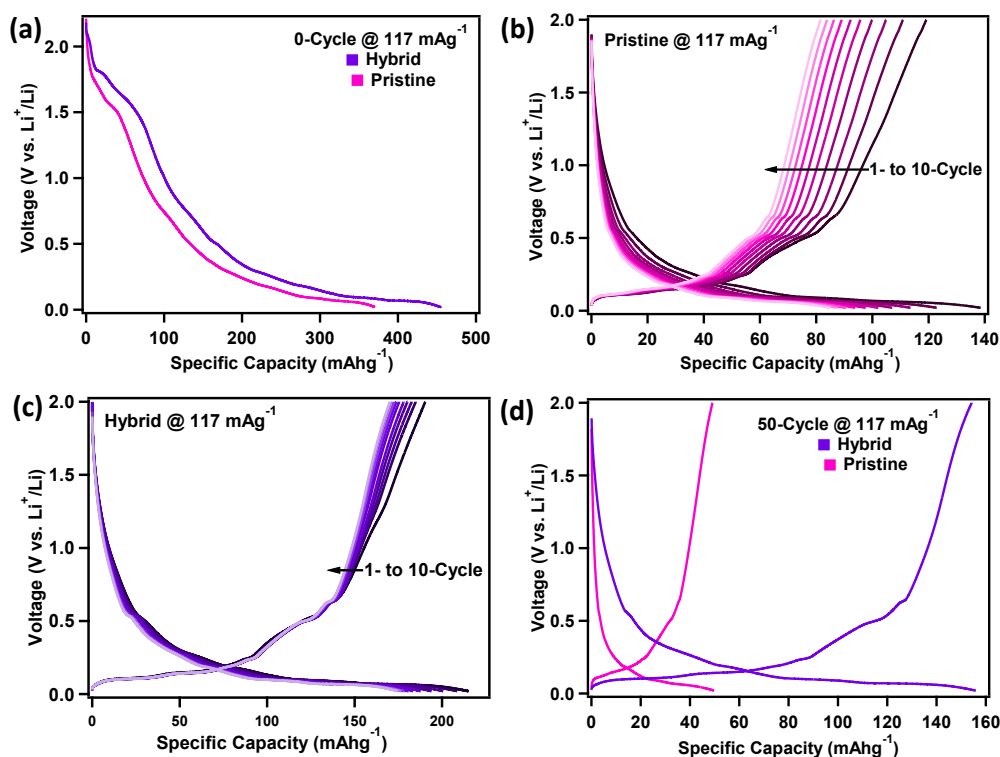


Figure 4.6 (a) Galvanostatic discharge profiles of hybrid and pristine LIBs measured at a current density of 117 mA g⁻¹ for 0th cycle. Galvanostatic charge-discharge profiles of hybrid and pristine LIBs measured at a current density of 117 mA g⁻¹ for (b-c) 1 to 10-cycles. (d) 50th cycle.

GCD curves for freshly prepared pristine perovskite and perovskite-MoS₂ hybrid LIBs are recorded at current density of 117 mA g⁻¹ for 0.02-2.0 V (vs Li/Li⁺) voltage window. The GCD curves for pristine and hybrid LIBs have shown voltage plateau region which are closely matching with the redox peaks observed in their corresponding CV plots. Here, pristine and hybrid LIBs have shown 370 mAh g⁻¹ and 455 mAh g⁻¹ specific capacity in first discharge (0th cycle) at current density of 117 mA g⁻¹ (**Figure 4.6a**), whereas in subsequent cycle (1st) the discharge specific capacity reduced to 138 mAh g⁻¹

and 215 mAhg⁻¹ respectively due to inability in removing the complete Li-ions inserted during the first discharge as well as due to reduction of electrolyte and formation of an SEI layer between electrode and electrolyte interface (**Figure 4.6b-c**) [Jadhav et al., 2014, 2016; Lim et al., 2019]. Moreover, as observed in the first 10 GCD cycles (2nd-10th cycles), the capacity is found to be fairly stable for the hybrid LIB compared to its pristine counterpart which has shown a significant drop in capacity while the redox potentials remain unchanged.

4.5.3 Rate cycling performance for pristine and hybrid LIBs

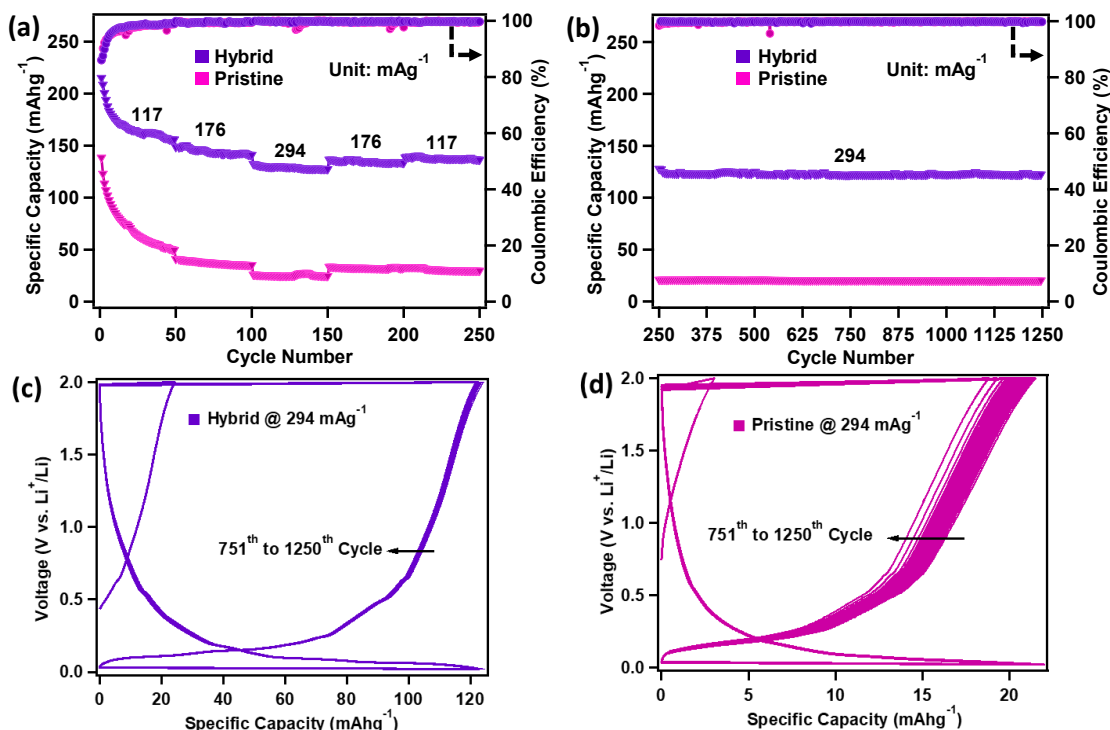


Figure 4.7 (a) Rate cyclability performances for hybrid and pristine LIBs measured at different current rates. (b) GCD cycle performances of hybrid and pristine LIBs at a current density of 294 mA g⁻¹ for 1000 cycles. Last 500 GCD profiles (751st - 1250th cycles) of (c) hybrid LIB and (d) pristine LIB recorded at current density of 294 mA g⁻¹ after rate cyclability test.

The rate cyclability performance of pristine and hybrid LIBs are investigated under different current rates over 250 cycles by a multiple step galvanostatic strategy for the 0.02-2.0 V (vs Li/Li⁺) voltage window as illustrated in **figure 4.7a**. Herein, 50 GCD cycles each were recorded to determine the discharge specific capacity for both LIBs at current densities of 117 mA g⁻¹, 176 mA g⁻¹ and 294 mA g⁻¹ and reversed back to 117 mA g⁻¹ followed by 176 mA g⁻¹. For the initial GCD cycles, the rapid capacity fading is observed in pristine LIB with specific capacity dropped to 49.70 mAhg⁻¹ on 50th cycle, suggesting capacity retention of 36.0 % (**Figure 4.6d, blue curve & Figure 4.7a**). Whereas the hybrid LIB has demonstrated slow capacity fading with specific capacity dropped to 156 mAhg⁻¹ on 50th cycles, suggesting capacity retention of 72.6 % (**Figure 4.6d, magenta curve & Figure 4.7a**). As the current density increased to 176 mA g⁻¹ and 294 mA g⁻¹, the hybrid LIB showed an average specific capacity of 144.46 mAhg⁻¹ (capacity retention: 94.95 %) for 51-100 cycles and 129.17 mAhg⁻¹ (capacity retention: 96.36 %) for 101-150 cycles respectively. In contrast, pristine LIB showed significantly lower average specific capacities of 37.48 mAhg⁻¹ (capacity retention: 85.53 %) for 51-100 cycles and 25.60 mAhg⁻¹ (capacity retention: 92.77 %) for 101-150 cycles respectively at corresponding current densities. Next, when the current density is reduced back to 117 mA g⁻¹, after exposure to high current densities, the average specific capacity of hybrid LIB recovered to 138.03 mAhg⁻¹ (capacity recovery: 96.36 %) as observed for 201-250 cycles, whereas the pristine LIB has not shown any capacity recovery after exposure to 176 mA g⁻¹. Followed by the rate cyclability measurements, the same cells were operated at a current density of 294 mA g⁻¹ for the next 1000 GCD (251-1250) cycles under same voltage window (**Figure 4.7b**). Both hybrid and pristine LIBs have demonstrated highly stable performance and

showed discharging specific capacities of 122 mAhg⁻¹ and 20.19 mAhg⁻¹ for 1250th cycle with corresponding coulombic efficiencies of 99.71% and 99.80% respectively. Additionally, it is observed that the charge-discharge voltage plateaus are clearly visible for the hybrid LIB when operated at high current rate of 294 mA g⁻¹ for 1000 cycle (**Figure 4.7c**), whereas pristine does not show the clear signature of such plateaus (**Figure 4.7d**). The inferior performance of pristine RP perovskite electrode is majorly attributed to the perovskite material stability issues in the liquid electrolyte (LiPF₆ 1M) environment, leading to the solvation of organic moiety (BA and MA) which ultimately destroy the perovskite crystallinity, as reported earlier by us [Ahmad et al., 2018; Mathieson et al., 2021b]. Whereas the superior performance of RP perovskite-MoS₂ hybrid electrode is attributed to the enhanced perovskite crystallinity, interfacial stability as well as improved charge transport due to the formation of perovskite-MoS₂ heterostructure. As we reported earlier, such heterostructures are formed by the heterogenous nucleation of perovskite microcrystals due to the presence of few layer MoS₂ nanoflakes [Ansari et al., 2023a; Liu et al., 2020].

4.5.4 EIS for pristine and hybrid LIBs

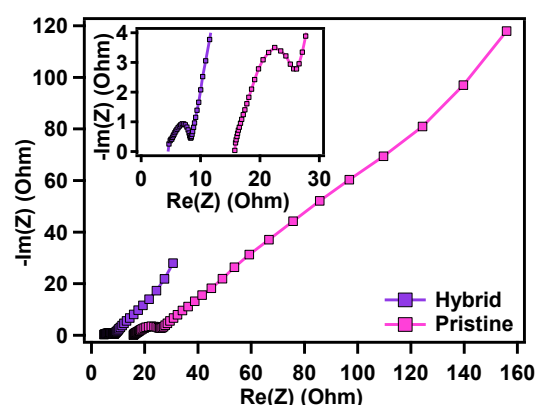


Figure 4.8 EIS spectra of hybrid and pristine LIBs

To investigate electrode kinetics, electrochemical impedance spectroscopy (EIS) measurements were carried out for pristine and hybrid LIBs on the same LIBs (after rate cyclability test) for AC current and frequency ranging from 1 MHz to 0.01 Hz with voltage amplitude fixed at 10 mV (**Figure 4.8**). The series combination resistances (R_s : represents current collector active material interface (CCAMI) and electrolyte resistance) for pristine and hybrid electrodes are found to be 15.8 Ω and 4.5 Ω respectively, whereas charge transfer resistances (R_{ct} : represents charge transfer in the electrodes) are found to be 10 Ω and 3.75 Ω respectively [Ventrapragada et al., 2018]. The decreased values of R_s and R_{ct} corresponding to the hybrid electrode shows efficient charge transport across RP perovskite-MoS₂ electrode due to the formation of heterostructure as discussed above.

Table 4.1 Comparison of electrochemical performance of demonstrated (BA)₂(MA)₃Pb₄I₁₃-MoS₂ hybrid LIB 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)	Ref.
(CH) ₂ PbI ₄ : PCBM/rGO: PVDF (80:10:10) on Cu; LIB	Li-metal	1 M LiPF ₆ , EC:DEC (1:1 v/v)	~100	~25 and ~25 % after 2 cycles	30	0.0-2.0	[Ahmad et al., 2018]
(CH) ₂ PbI ₄ : PCBM/rGO: PVDF (80:10:10) on Cu; LIB	Li-metal	1 M LiPF ₆ , EC:DEC (1:1 v/v)	~100	~25 and ~25 % after 2 cycles	30	0.0-2.0	[Ahmad et al., 2018]

							2018]
Cs ₂ Bi ₂ I ₉ ; PCBM: PVDF (80:10:10) on Cu ; LIB	Li-metal	1 M LiPF ₆ in EC:DMC (1:1 v/v)	~413	~60 and ~15 % after 50 cycles	50	0.01– 2.5	[Tewari et al., 2021]
DAPbI: CNT: PVDF (60:30:10) on SUS 304 SS foil ; LIB	Li-metal	1 M LiTFSI DOL:DME (1:1 v/v)	~78 and	~21 and ~27 % after 20 cycles	20	1.6-2.5	[Chen et al., 2022a]
(iBA) ₂ (MA) ₃ Pb ₄ I ₁₃ on PTFE coated Carbon Cloth ; AIB	Al-metal	AlCl ₃ /EMIC= 1:3	~275	~173 and ~63 % after 50 cycles	200	0.4-1.2	[Wu et al., 2023b]
(BA) ₂ (MA) ₃ Pb ₄ Br ₁₃ : Super-P: PVDF (85:5:10) on Cu ; LIB	Li-metal	5 M LiTFSI in EC:PC (1:1 v/v)	~275	~80 and ~29 % after 99 cycles	30	0.1-2.7	[Mathieson et al., 2021b]
(PA) ₂ (MA) ₃ Pb ₃ Br ₁₀ : Super-P: PVDF (70:15:15) on Cu ; LIB	Li-metal	1 M LiPF ₆ EC:DEC (1:1 v/v)	~175	~35 and ~20 % after 10 cycle	425	0.1-1.5	[Ramirez et al., 2018]
(BA) ₂ PbBr ₄ : Super-P: PVDF (60:30:10) on Cu ; LIB	Li-metal	1 M LiPF ₆ in EC:DMC (1:1 v/v) with 5% FEC	~510	~213 and ~42 % after 50 cycles	100	0.01-2.5	[Tathavadekar et al., 2017]
(BA) ₂ (MA) ₃ Pb ₄ I ₁₃ :MoS ₂ : rGO: Super P, PVDF (84.6:0.4:5:3:7) on Cu ; LIB	Li-metal	1 M LiPF ₆ in EC:DMC (1:1 v/v)	~215	~156 and ~73 % after 50 cycles	117	0.02-2.0	This Chapter

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