Are Halide-Perovskites Suitable Materials for Battery and Solar-Battery Applications—Fundamental Reconsiderations on Solubility, Lithium Intercalation, and Photo-Corrosion

Jan Büttner, Taisia Berestok, Stephan Burger, Manuel Schmitt, Michael Daub, Harald Hillebrecht,* Ingo Krossing,* and Anna Fischer*

1. Introduction

The field of photoelectrochemical energy conversion and storage has received great attention over the last couple of years.[1–7] The conceptual idea dates back to the 1970’s and is closely related to the origins of photoelectrochemical water splitting and the later developed dye sensitized solar cells. The employed systems range from dye sensitized solar cells (DSSC), perovskite solar cells (PSC), to organic solar cells (OPV) and classical silicon-solar cells (Si-SC) for energy conversion. Energy storage has among others been realized by capacitors, supercapacitors, Li-ion batteries, redox flow batteries, and water splitting, in various modes of integration.[8–17]

The potential of photoelectrochemical energy conversion and storage is the temporal decoupling of the availability of solar energy and the need for the consumption of electricity. This is very desirable because solar energy is only available during the day, but electrical energy is needed around the clock for almost every aspect of technology in nowadays society. As a consequence, an energy storage system is required to ensure continuous energy availability.

A common solution to ensure sustained energy availability, therefore, is a battery connected to a photovoltaic (PV) system via wiring. This architecture, if set up as a four-electrode system in which no integration whatsoever is present,[18,19] is referred to as integration mode I (Figure 1a).[20] The obvious merits of integration of these two functionalities, i.e., solar energy harvesting and electrochemical energy storage, into one device are reduced...
cost, less internal power losses, and reduced device volume and footprint. The next step of integration is a three-electrode monolithic architecture with one shared electrode between energy conversion and storage system, called integration mode II (Figure 1b).[21,22] The highest possible integration level reachable is a two-electrode system with one multifunctional photo battery electrode capable of energy conversion (PV-functionality) and storage (battery functionality) at the same time and place which is called integration mode III (Figure 1c).[23,24]

The obvious challenge, especially for a fully integrated two-electrode mode III device is finding a suitable material providing all the abovementioned functionalities at once. One candidate proposed are organic–inorganic lead halide perovskites. These materials are known to be very promising and contribute to the fast development of perovskite solar cells (PSC), which after only little more than 10 years of development outperform classic Si-solar cells on a lab scale.[25] During the last years, several studies also have investigated different halide perovskites as LIB active materials,[26–28] their general behavior with respect to Li-ion intercalation and/or conversion chemistry,[29–31] their Li⁺-conduction behavior,[32,33] and their electrochemical as well as dissolution stability.[34,35]

With the aim to go beyond simple energy storage, an organic–inorganic lead halide 2D perovskite, namely 2-(1-cyclohexenyl) ethyl ammonium lead iodide (in short CHPI), was recently introduced by Ahmad et al. as multifunctional photoelectrode material for a Li-ion rechargeable photo battery, where reversible photo-induced (de-)intercalation of Li-ions from/into the perovskite and thereby photo charging of the battery was claimed.[36] Compared to the as-synthesized CHPI powder (Figure S1b, Supporting Information), where the crystallographic orientation is identified up to the 12th order, whereas the other reflections are not observable.[37] In this presented mode 3 configuration, the CHPI-based photoelectrode, deposited on a transparent fluorine doped tin oxide (FTO) substrate, is assembled in a battery type configuration as cathode with a Li-metal counter electrode as anode, separated by a carbonate-based electrolyte-soaked separator. Recently another similar report introducing cesium bismuth iodide (Cs₃Bi₂I₉) as multifunctional photoelectrode material for a Li-ion rechargeable photo battery was published by Tewari et al.[37]

In the present work and based on the somehow conflicting literature reports on organic–inorganic lead halide perovskites for Li-ion rechargeable batteries and Li-ion rechargeable photo-batteries, we revisited the (photo)electrochemical behavior of CHPI and reexplored its applicability as a multifunctional photoelectrode material for highly integrated Li-ion based mode III photobatteries. We investigated its (photo)electrochemical behavior in very polar carbonate-based electrolytes, typically used in LIBs (and previous reports) and a newly developed low polarity electrolyte, to probe CHPI-stability against dissolution, possible Li-intercalation, and photo-assisted deintercalation (photo charging). In addition, the general behavior of CHPI under illumination and in contact with liquid electrolyte was assessed.

2. Results and Discussion

First, we synthesized and characterized model thin films of polycrystalline CHPI of molecular formula (C₆H₉C₂H₄NH₃)₂PbI₄— a Ruddlesden–Popper (RP) phase often referred to as organic–inorganic lead halide 2D perovskite, and investigated their applicability as multifunctional photoelectrode materials for mode 3 photobatteries.

2.1. Thin film Synthesis and Characterization

The model CHPI thin films for the (photo)electrochemical characterization were synthesized by spin coating on FTO-coated glass substrates (see Experimental Section for details). As demonstrated by SEM (top view images), the resulting homogeneous polycrystalline thin films are composed of micrometer sized domains with rod-shaped submicron-sized surface topography (Figure 2a and Figure 2).

Bragg–Brentano X-ray diffraction (BB-XRD) reveals highly oriented crystal domains (Figure 2e). The (00l)-reflections can be identified up to the 12th order, whereas the other reflections are not observable.[38] Compared to the as-synthesized CHPI powder (Figure S1b, Supporting Information), where the crystal domains are more randomly distributed, the domains in the thin films grow highly parallel to the substrate plane.
UV–vis reveals an optical bandgap of $E_g = 2.51$ eV and a very strong excitonic absorption peak at $E_{\text{Exciton}} = 2.38$ eV (Figure 2c,d). Both are in line with previously reported values for CHPI, although the excitonic binding energy of 130 meV (roughly five times the thermal Energy at 298 K $k_B T = 26$ meV) is lower than previously reported values between 200 and 300 meV.[39,40] Compared to the powder sample both absorption edges have increased by $\geq 100$ meV (Figure S1d, Supporting Information) probably due to the enhanced quantum confinement effect of the thin aligned platelet-like domains.[41] Due to the Shockley–Queisser limit the measured bandgaps would result in maximum conversion efficiencies of $\approx 12.5$–$15\%$.[42]

### 2.2. (Photo)electrochemical Characterization

The as synthesized CHPI thin films were characterized in a home build photo battery electrochemical cell to exclude oxygen and moisture (Figure 2f; Figure S8, Supporting Information). As counter electrode we used lithium metal, as separator a Freudenberg non-woven polymer thin film and as electrolyte 1 m LiPF$_6$ in EC:DMC, 1:1, v:v (short: LP30), a very commonly used battery electrolyte (for details see Experimental Section).[43,44]

Unfortunately, in the assembled photo battery cell the CHPI is immediately dissolved upon contact with the electrolyte (Figure 3a; Inset). It is important to mention, that no reports on this type of behavior, i.e., dissolution in polar battery electrolytes, has been documented yet, be it for CHPI or other halide perovskite materials, previously investigated in Li-ion photo batteries or Li-ion batteries.[36] The polarity of LP30 (dielectric constant around $\varepsilon_r \approx 30$) seems high enough to dissolve the CHPI at room temperature before any protective solid electrolyte interface (SEI) can form. If compared to dimethylformamide (DMF) (dielectric constant around $\varepsilon_r = 36.5$), the solvent used for CHPI thin film preparation, this result is not
very surprising though. To get a quantitative picture, we further investigated the solubility of CHPI in LP30 and found it to be ≈42 mmol L⁻¹ (details Figure S2, Supporting Information).

Nevertheless, we investigated the cell’s dark electrochemistry by covering the electrode and recording a cyclic voltammogram (CV) (Figure 3a). It clearly shows at least two partially reversible redox systems. We assign those to the I⁻/I₃⁻ system for the signal ≈3.1 V versus Li/Li⁺ and the combination of the RNH₃⁺ system and possibly the redox reactions of PbₓIᵧ species ≈2.1 V versus Li/Li⁺.[47–50] Blending the CHPI thin film with carbon black, (10 wt.%), similar to Ahmad et al.,[36] did not improve the situation and also resulted in dissolved CHPI with a similar CV (Figure S4c,d, Supporting Information).

To further investigate the solution electrochemistry of the CHPI-constituents we investigated the respective salts, 2-(1-cyclohexenyl)ethyl ammonium iodide (CHAI) and lead iodide (PbI₂), separately. Figure 3b–d shows the electrochemical behavior of a bare FTO-electrode in combination with 18.8 mmol L⁻¹ CHAI in LP30 (CHAI-electrolyte, Figure 3b), 9.4 mmol L⁻¹ of lead iodide in LP30 (PbI₂-electrolyte, Figure 3c) and pristine LP30 (Figure 3d). In the CHAI electrolyte, the Γ⁻/I⁻ redox system is present ≈3.15 V versus Li/Li⁺ and appears to be more reversible compared to the dissolved CHPI film in Figure 3a. Also, a further shift of the oxidative and reductive waves is visible for consecutive cycles, which is an indication for an irreversible consumption of one of the species. Regarding the second redox system ≈2.3 V versus Li/Li⁺, we assume it to be associated to RNH₃³⁻. It can be seen that this redox system is disappearing completely over the course of 4 cycles, indicating an irreversible process.

In the PbI₂-electrolyte (Figure 3c), compared to the CHAI-electrolyte (Figure 3b) the oxidative peak of the Γ⁻/I⁻ redox system ≈3.15 V versus Li/Li⁺ is shifted to a marginally lower voltage, the current density has more than halved and the reductive peak has almost completely vanished, being even less pronounced than for the dissolved CHPI (Figure 3a). We attribute this behavior to the possible presence of lead-(poly)iodide species in solution, which form after I⁻ has been oxidized to I₃⁻ and thereby partially prevent the reduction of the I₃⁻ ion in the cathodic sweep. For the comparison it is important to emphasize, that the initial I⁻ concentration is the same for both measurements in Figure 3b,c. The second redox system, coincidentally also ≈2.3 V versus Li/Li⁺, shows two reductive peaks at 2.16 and 2.24 V versus Li/Li⁺ respectively. Since no RNH₃⁺ is present in the electrolyte and the reductive peaks are more stable than in Figure 3b we suggest that both peaks indicate the reduction of different PbₓIᵧ species. The oxidative peak is very broad and shows the redox system to be not fully reversible. While the reductive peak at 2.24 V versus Li/Li⁺ is decreasing over 4 cycles, the reductive peak at 2.16 V versus Li/Li⁺ is increasing, which in combination with the constant oxidation peak hints to a coincidental overlap of at least two oxidation reactions.

In Figure 3d the cyclic voltammogram of the pristine LP30 is shown depicting no faradaic (explanation see Supporting Information) reactions whatsoever, confirming the base electrolyte to be electrochemically silent and stable in this potential window.
Hence all signals seen in Figure 3a–c originate from CHPI, CHAI or lead iodide in solution. Cycling to more reductive potentials below 2.0 V versus Li/Li$^+$ causes the FTO substrate to turn black, which indicates reductive degradation of the FTO, similar to observations in other electrolytes before (Figure S3d, Supporting Information).[51]

Since CHPI is dissolving in the classical carbonate based high polarity battery electrolytes (e.g., LP30) a proper assessment of its potential Li$^+$-intercalation capabilities in these is not possible. Consequently, we used a new low polarity electrolyte for Li-ion batteries based on Li$^+$ coordinated by DME in a 1:2 stoichiometry. Hence, this newly developed electrolyte by Burger and Krossing et al. (to be submitted) is based on Li(DME)$_2^+$ as diffusing entity in the polar aprotic, but low viscosity solvent o-DFB ($\varepsilon_r$ = 13.8) in combination with the lithium salt of the weakly coordinating anion [pf]$^-$ ($=\text{[Al(OR$_3$)$_4$]}^-$ with $R^2 = \text{C(CF}_3)_2$) and fluoroethylene carbonate (FEC) as SEI formation agent (short: Li[pf]$^-$-o-DFB, details see Experimental Section and Supporting Information).[52–54] With this new low polarity electrolyte, we were able to build a cell in which the CHPI film electrode was not dissolving immediately after contact with the electrolyte (see Figure 4b; Inset).

Figure 4a shows CV traces of spin coated CHPI on FTO in Li[pf]$^-$-o-DFB electrolyte. When compared to the previous measurements in the very polar LP30 electrolyte (Figure 3a–c), the redox peaks, visible before in the polar LP30 electrolyte, are almost invisible in Li[pf]$^-$-o-DFB. For better comparison Figure 4b shows a zoom of Figure 4a. It reveals only a minimal oxidation of $\Gamma$ to $\text{I}_3^-$ above 3.2 V versus Li/Li$^+$ and a very sluggish reduction back to $\Gamma\approx2.4$ V versus Li/Li$^+$ with an overpotential of more than 500 mV. Figure 4c shows a CV of blank FTO-glass in Li[pf]$^-$-o-DFB. While the current densities here are also very low, the complete absence of any faradaic reaction is evident. For easier comparability Figure 4d shows the graph from Figure 3a again. From these data, we conclude that the same partly irreversible oxidative process in the voltage range of the $\text{I}_2^-/\text{I}_3^-$ system occurring in the LP30, still takes place in the low polarity Li[pf]$^-$-o-DFB, indicating minuscule dissolution of CHPI, even in Li[pf]$^-$-o-DFB.

At this point we conclude there is a solid CHPI phase after contact with Li[pf]$^-$-o-DFB that can be investigated towards its Li$^+$ intercalation ability. Since the CV investigation did not provide any evidence for Li-ion intercalation a galvanostatic charge discharge with very low current was attempted.

In Figure 5a a galvanostatic discharge–charge with a current density of $\pm250$ nA cm$^{-2}$ shows no faradaic reductive current between open circuit voltage (OCV) (2.7 V versus Li/Li$^+$) and 2.0 V versus Li/Li$^+$ (lower cut-off voltage) for the initial discharge sweep. Since the pristine material is free of intercalated Li$^+$ (i.e., charged with respect to a Li-ion related energy storage process) one would expect a Li$^+$ intercalation process associated with a voltage plateau here. Its absence is a very strong indicator, that no Li$^+$ intercalation is possible in CHPI. Further “discharge” was not attempted, because FTO showed reductive degradation below 2.0 V versus Li/Li$^+$ (Figure S3d, Supporting Information). For the first charge sweep of the CHPI an oxidation of $\Gamma$ to $\text{I}_3^-$ = 3.3 V versus Li/Li occurs, confirming the

![Figure 4](image-url)
findings from cyclic voltammetry (vide supra, Figure 3a–c; Figure S4d, Supporting Information). Since the process is at least partly irreversible (degradative) we stopped the “charge” after 2 h, but the process will carry on as long as there is I⁻ left to oxidize (See Figure S6a, Supporting Information – 15 h “charge”). For a compact film with a thickness of 1.3 µm (which is in the range of results received by profilometer measurements), the complete consumption of CHPI would take ≈33.5 h assuming the oxidation of I⁻ to I₃⁻ takes place. For the following “discharge” there is a faradaic plateau, starting at ≈2.8 V versus Li⁺/Li. We want to stress, that this plateau is not due to Li⁺ intercalation but occurs because of I⁻ reduction to I⁻ in solution, possibly redepositing some of the beforehand destroyed CHPI, while definitely not being fully reversible. For the next cycle we adjusted the upper cut-off voltage to be at 3.3 V versus Li⁺/Li⁺ to limit the iodide oxidation and as a result both plateaus ≈3.3 V versus Li⁺/Li⁺ and <2.8 V versus Li⁺/Li are diminished immediately and disappear almost completely in subsequent cycles, further supporting a sole responsibility of the I⁻/I₃⁻ redox pair for the faradaic plateaus appearing in these galvanostatic experiments. Figure 5b shows a similar measurement with a blank FTO electrode for comparison and purely capacitive behavior is displayed, as no faradaic plateau is visible (for further explanation about capacitive and faradaic behavior see Supporting Information).

As no faradaic process related to Li-ion-(de)intercalation could be detected in both CV and galvanostatic charge discharge, we come to the conclusion that Li-ion intercalation is not taking place in CHPI. Further cyclic voltammograms with different scan rates (1–100 mV s⁻¹) underline the purely capacitive (explanation see Supporting Information) behavior of the CHPI on FTO in Li[PF₆]-o-DFB in the potential window between 2.3–3.2 V versus Li⁺/Li⁺, which is also confirmed by PEIS (see Figure S7, Supporting Information) and the oxidation of I⁻ to I₃⁻ >3.2 V versus Li⁺/Li⁺ (vide supra, Figure 3a–c).

To investigate the behavior under photoelectrochemical conditions we performed a similar experiment with intermittent illumination. Figure 6a shows a galvanostatic discharge–charge
Figure 7. Schematic of CHPI behavior for different scenarios. a) Simplified schematic CHPI structure. b) CHPI dissolution in polar solvents. c) Stable CHPI in low polarity electrolyte, but no quantitative Li⁺ intercalation, needed for relevant energy storage, occurs. d) Reductive electrochemical degradation of CHPI with Pb formation. e) Photo corrosion of CHPI under illumination.

with a current density of ± 250 nA cm⁻² with intermittent illumination (AM 1.5 G, 100 mW cm⁻²) indicated by the orange areas. The graph comprises five sections. Section 0 shows the OCV (=2.8 V versus Li/Li⁺) before the measurement starts and the first dark discharge showing no faradaic reductive plateau between OCV and 2.3 V versus Li/Li⁺ (lower cut-off voltage; section 0 not indicated because it is very narrow). Section I shows the first illumination period, while applying a charging current. An instantaneous voltage increase to 3.39 V versus Li/Li⁺ upon illuminating the sample is followed by a temporary decrease to 3.3 V versus Li/Li⁺. A constantly rising voltage plateau between 3.3 V versus Li/Li⁺ and 3.4 V versus Li/Li⁺ (upper cut-off voltage) appears over the course of 4 h, indicating a much faster depletion of oxidizable species, than expected. This behavior is most likely caused by photo degradation of the perovskite, namely oxidative photo corrosion of the iodine via the simplified Equation 1.[53]

\[ 3I^- + hv \rightarrow I_3^+ + 2e^- \]  

(1)

Section II shows the second discharge in dark with a very broad reductive plateau between 3.0 and 2.45 V versus Li/Li⁺ in absence of illumination, comparable to the plateaus in Figure 5a and Figure S6a (Supporting Information). Section III shows the second and third charge and discharge; all are illuminated. During discharging under illumination (section III – middle), for ten hours, a plateau stretches from ~3.3 V versus Li/Li⁺ to ~3.0 V versus Li/Li⁺, again indicating a constant photo-oxidation (see Equation 1) replenishing I₃⁻, which is electrochemically reduced causing the plateau. These findings match very well with the solution chemistry of CHPI we investigated previously (vide supra, Figure 3a–c). A third discharge, again under illumination (section III – right), shows the same behavior, but the faradaic plateau immediately collapses, once the illumination stops (end of section III, after ~75 000 s).

Section IV shows a series of discharge/charge cycles in dark (Figure 6b is a zoom in of section IV) measured in continuation of section III. The faradaic elements (small plateaus near the cut-off potentials) disappear almost completely and shrink with every cycle until the charge discharge behaves purely capacitive (details see Supporting Information) once more, similar to the behavior in completely dark conditions (Figure 5a). This indicates the irreversible nature of these redox reactions. It is important to mention here that the yellow CHPI perovskite coating deposited on the FTO substrate almost completely disappeared over the course of the experiment, which confirms the photo-induced oxidation/dissolution of the material and hence the release of lead and iodine-containing redox active species. This photo-induced degradation also occurs within any external voltage applied, i.e., under OCV conditions and under illumination, as demonstrated in Figure S8 (Supporting Information). In conclusion the faradaic processes in Figure 6 are caused by a combination of (photo)electrochemical oxidation and electrochemical reduction of CHPI and are not a sign of a photo-assisted charge but rather a sign of an irreversible perovskite degradation (Figure 7e). To further corroborate the degradation mechanism of CHPI we performed DFT and ccsd(t) calculations describing the dissolution of CHPI in EC:DMC (I:1, v:v). We propose a degradation via the dissolved [PbI₃]⁻ anion, which dissociates in solution in a small degree into [PbI₄]⁻ + I⁻. The standard Gibbs energy in EC/DMC-solution for this reaction is ΔrG°(solv) = + 18.1 kJ mol⁻¹, resulting in an equilibrium constant of K(solv) = 7 × 10⁻⁴ (Details see Supporting Information). Hence, by this process iodide is always present in electrochemically active concentrations that for any electrochemical cycling process is high enough to be continuously withdrawn from the equilibrium.

In light of our results, we come to the conclusion that reported cases of multifunctional organic–inorganic halide perovskite based Li-ion rechargeable batteries in combination with liquid electrolytes reported in literature are at least very doubtful. In one case the supposed “photo-charge” was recorded by measuring the OCV between the perovskite and the lithium metal electrode, while illuminating the perovskite.[36] If an electronic device like a multimeter or a potentiostate (which was used in that case) is measuring OCV, the two electrodes are connected by a very large resistor (1 Ω, for a VMP-3 from BioLogic). This excludes any relevant current flow through the outer wires connecting the two electrodes and thereby makes any claimed photo-charging impossible. At
best a local photo-induced redox reaction occurs at the “multifunctional” electrode. Further every halide perovskite (2D and 3D) synthesized by i) dissolving its educts in a polar solvent like DMF and ii) subsequent evaporation of the solvent (like it is typically done during spin coating) will have severe solubility issues in polar battery electrolytes (Figure 7b). This includes most of the commonly used iodide and bromide comprising perovskites and the structures that use both halides.\(^{[56]}\) Regarding the usage as Li-ion battery electrode, recent studies also report severe dissolution of other 2D Ruddlesden Popper perovskite phases (comprising iodide and bromide) to take place in the presence of LP30 electrolyte, confirming our findings.\(^{[57]}\) Similarly to our approach chosen here—the development of a low polarity electrolyte compatible with organic–inorganic halide perovskites—interface engineering with electrolyte stable surface coatings could alleviate the perovskites instability issues as we have shown here with a low polarity electrolyte (Figure 7c), but this would not change the inability of the substate perovskite phase to actually store relevant amounts of charge via a reversible Li\(^+\) ion intercalation mechanism, as will be discussed later. In terms of the stability, the possibility to use a solid state electrolyte (in the referenced case a polyethylene oxide :LiTFSI polymer electrolyte fabricated from acetonitrile solution) to lithiate a 3D halide perovskite has been investigated recently.\(^{[58]}\) The amount of lithiation achieved was in the range of 10\(^{-3}\) mAh g\(^{-1}\), five orders of magnitude lower than observed for typical battery materials (compare Figure S10d, Supporting Information), and the authors themselves describe the process as “doping”. Unfortunately even this small amount of lithiation is not fully reversible, which is ascribed by the authors to the “oxidation of halide or methylammonium ions” taking place.

Finally there is a much more general point that is essential to achieve energy storage via ion intercalation. The host structure needs to have a redox active species that accepts and eventually releases electron density upon inter- and deintercalation (e.g. Co\(^{3+}/\text{Co}^{4+}\) in case of LiCoO\(_2\)). In case of a positive battery material (cathode material) the material is charged by concomitant oxidation (removal of electrons) and Li\(^+\) deintercalation and discharged by the reverse process. That means a material without any Li\(^+\) is in a charged state after assembling a cell against a lithium metal counter electrode. In this state, the material could be discharged if it would accept electrons. The subsequent charge would reverse this process. In a halide perovskite ABX\(_3\) or the 2D variant A\(_2\)BX\(_4\), the candidates to accept these electrons are the A and/or B cation. In case of a photo battery, where the multifunctional electrode material must be able to harvest energy and store it at the same time, one of these constituents must be a reversible redox system stable in its structure. This implies the bulk perovskite crystal structure, determining the semiconducting properties, must stay intact. Any metal cation, that has no available redox state that is not zero (metallic form = destruction of the perovskite), below the one that is naturally occurring in the halide perovskite structure, is unable to accept electron density, while maintaining the perovskite structure. For a lead halide perovskite system, this would imply, e.g., a Pb\(^5+\)/Pb\(^{2+}\) system or any other redox state of Pb\(^+\) with 0 < x < 2. With this prerequisite intercalation and not alloying between Li and Pb could occur. This would require at least a partial presence of Pb\(^+\) (or Pb\(^x+\)) like indicated by Dawson et al.\(^{[29]}\) based on calculated Bader-charges. This however needs further investigations and proof, since Pb\(^+\) is clearly not a common oxidation state lead is found in. The alternative would be to use a second B cation or the A cation to store the charges. Any A cation, be it organic or inorganic, that does not allow any reversible redox reaction will not work. This includes every ammonium cation and every alkali cation. Alternative B cations to Pb\(^{2+}\), that are found in literature and will not work comprise but are not limited to Bi\(^{3+}\), Sn\(^{2+}\). This is why we are convinced that the above discussed state-of-the-art perovskites are not usable to store energy via an intercalation process.

In order to act as a multifunctional photo battery material, that is able to perform a photo charge (charging current induced by illumination without external bias) several requirements are needed. The light absorbing (semiconducting) properties of the material in the initial state (free of Li\(^+\), see above) need to be retained during lithiation. If the semiconducting properties are lost completely, like it is the case during an energy storage process based on a conversion reaction subsequent photo charge is impossible. If lead halide perovskites are used as a LIB anode material (potentials lower than 1.1 V versus Li/Li\(^+\)), Pb\(^0\) is produced with irreversible decomposition of the perovskite (Figure 7d). The metallic lead then forms Li-Pb intermetallic compounds, which can be a partially reversible (non-intercalation based) Li-ion storage material.\(^{[31,59]}\) Even if this conversion would be completely reversible a photo charge is only possible, if the discharged (lithiated) compound is still a semiconductor (If the material just dissolves, as encountered in polar battery electrolytes, this is certainly not the case). Hence, at best some of the reported organic–inorganic lead halide perovskites are possible anode (negative electrode) conversion type electrodes, but these results have nothing to do with a multifunctional photo battery (cathode) material.

### 3. Conclusion

In conclusion we provide conclusive evidence that 2-(1-cyclohexenyl)ethyl ammonium lead iodide organic–inorganic lead halide 2D perovskite is soluble in polar carbonate based LIB electrolytes. When a suitable low polarity electrolyte stabilizing the material is chosen, no electrochemical evidence for Li\(^+\) intercalation was found for the CHPI electrode, but rather a purely capacitive behavior. Attempting an illuminated galvanostatic “charge” of the electrode in a photo battery setup, while in contact with the electrolyte leads to photo corrosion and subsequent dissolution of the CHPI phase. This oxidative corrosion can also be achieved by simply oxidizing the material in dark or just illuminating the material without any external voltage. These dissolved species give rise to faradaic plateaus, but are neither indicating any Li-ion-intercalation in a solid CHPI phase nor correspond to a photo or photo-assisted charge. The inherent chemical, electrochemical and photochemical instability of halide perovskites (especially iodide, and bromide containing compounds) and their incompatibility with a Li-ion based intercalation chemistry in our eyes disqualify these materials for any usage in a mode III photobattery system and further its use in direct combination with any polar liquid electrolyte based battery systems, at least if intercalation chemistry is targeted.
4. Experimental Section

Powder Synthesis: 2-(1-cyclohexenyl)ethyl ammonium iodide (CHAI) powder was synthesized by dissolving 2-(1-cyclohexenyl)ethyl amine (10.16 g, 97%, Sigma–Aldrich) in toluene (30 mL, Normapur, VWR) and slow dropwise addition of hydroiodic acid (15.54 mL, 57 wt.% in water, Acros), while keeping the mixture at room temperature with a water bath. After 30 min the water was removed thermally from the toluene–water azeotrope at 110 °C which left a white/brownish precipitate of CHAI. The product was washed with toluene and diethyl ether (99.7%, anhydrous, Sigma–Aldrich) several times and a white powder resulted (yield: 91.2%).

2-(1-cyclohexenyl)ethyl ammonium lead iodide (CHPI) was prepared by dissolving CHAI (5.23 g) and lead iodide (4.75 g, 99%, Sigma–Aldrich) in a 2:1 molar ratio in dimethylformamide (DMF) (6.88 mL, 99.8%, anhydrous, Sigma–Aldrich). Afterward the solvent was slowly evaporated (120 °C, 10⁻² mbar). The reaction yielded a yellow to orange powder (yield 96.6%). Characterization by XRD and SEM matched with expectations from literature (Figure S1, Supporting Information).

Spin Coating: CHAI (660.9 mg) and lead iodide (599.5 mg) in a 2:1 molar ratio were dissolved in a DMF (1.04 mL): dimethyl sulfoxide (DMSO) (0.26 mL) (>99.8%, <100 ppm water, Carl Roth) (4:1, v:v) mixture, to yield a 1 m solution. Fluorine doped tin oxide (FTO) coated glasses (2 cm x 2 cm, total thickness 1 mm, FTO coating sheet resistance: 7 Ω sq⁻¹) were cleaned in an ultrasonic bath for 15 min in acetone, ethanol, and water respectively and blown dry with a nitrogen stream after the last cleaning step. One hundred microliters of the slurry were spread on the FTO coated glasses, which were subsequently rotated with 1000 rpm for 10 s and 3000 rpm for 20 s. A post annealing at 100 °C for 10 min followed.

Doctor Blading: The slurry was prepared similarly to the spin coating solution, but carbon black (10 wt.%, Super C65, Timcal) was subsequently added to the solution and dispersed with an IKA Ultra Turrax Ball Mill at 6000 rpm for 10 min. The material is coated with a speed of 10 mm s⁻¹ and a blade height of 10 μm. The wet film was dried at 100 °C for 1 h and further at r.t. and under vacuum overnight.

Characterization: X-Ray Diffraction for powders and for thin films was measured on a Bruker D8-Discover in a Bragg–Brentano geometry with Cu Kα-radiation. Scanning electron microscope characterization was performed with a Hitachi field emission gun scanning electron microscope (FEG-SEM) SU8220 operated at low acceleration voltage of 1 kV. UV–vis characterization was performed with a Hitachi field emission gun scanning electron microscope (FEG-SEM) SU8220 operated at low acceleration voltage of 1 kV. UV–vis was measured on an Ocean Optics QE Pro with a deuterium and halogen light source in the range of 200 to 800 nm in transmission geometry for the thin films and reflection geometry for powders.

Electrochemical characterization was done with a BioLogic VSP potentiostat. Measurements were performed with a specifically self-designed photo battery electrochemical cell (Details see Supporting Information). As electrolyte 1 M LiPF₆ in ethylene carbonate/dimethylcarbonate (1:1, v:v, Sigma–Aldrich = LP30) and 0.2 M Lithium perchloratoxyaluminiate (Li[LiPF₆][Al(OR)₄]₂, R²⁻ = C(F₃CO)₂) Li[LiPF₆] in ortho-difluorobenzene (o-DFB): dimethoxyethane (DME): fluoroethylene carbonate (FEC) (59:0:2.6:1.0, v:v:v = Li[LiPF₆]:o-DFB) were used. Freudenberg non-woven polymer separator was used as separator. Lithium metal was used as counter electrode. CHPI coated onto FTO coated glass and CHPI/CB coated onto FTO coated glass were the samples investigated. All samples had the dimensions 2 x 2 cm. All cells were assembled inside an Argon-glovebox (O₂<0.1 ppm, H₂O<0.1 ppm). The illumination for the photoelectrochemical characterization of these cells was done with a LS2 LED-solar-simulator (Wavelabs, AM 1.5 G, 100 mW cm⁻², AAA).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2-(1-cyclohexenyl)ethyl ammonium lead iodide, Li-ion batteries, metal halide perovskites, organic–inorganic lead halide 2D perovskites, photo-rechargeable batteries

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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