

Two-dimensional Halide Perovskites Based Supercapacitors: A Review on Synthesis, Properties, and Stability

Abstract

To gain a better understanding of the factors influencing the performance of 2-D perovskites-based supercapacitors, as well as the obstacles still to be overcome and potential avenues for future research, this article will review and analyze the current literature on the stability of these devices. Organic-based materials have been extensively studied in supercapacitors because of their high capacitance and capacity to store charge through quick and reversible redox reactions. Given that high power densities are directly correlated with the rate of charge/discharge, which is based on the kinetics of the redox reactions, this is an essential component of the super capacitive performance. This review article centers on a thorough overview of the most recent advancements in 2D HPs, a material that has shown great potential as a supercapacitor but has received relatively little attention up to this point.

Thus, the significance and fascinating feature of 2D halide perovskites as supercapacitor materials for their exciting potential applications in energy storage in the future are covered in detail in this review.

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1. Introduction

Researchers from a wide range of disciplines have long been interested in two-dimensional (2D) layered materials. This is because of the highly anisotropic structure of the 2D materials, which endows them with special qualities akin to those of single crystal materials. Electrochemical supercapacitors have been created to date using a variety of 2D materials (SCs). SCs have significantly improved over time, offering superior energy storage choices for a wide range of electronics and extensive applications. The primary problem with SCs, however, is that their energy density and storage capacity are significantly lower than those of secondary batteries because they can only store charge using the Nernst equation.¹ Schon et al. (1997) found that $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ had a high capacitance per unit area of $610 \mu\text{F}/\text{cm}^2$ at 2V in an aqueous electrolyte. This value is significantly higher than that of commercially available SCs. This substance is a member of the perovskite family, whose ferroelectric and dielectric qualities have been the subject of decades of research. In recent times, there has been extensive research on a novel class of perovskites called organic-inorganic hybrid metal halide perovskites (OIHMHPs) due to their high efficiency in solar cells. After just 11 years of study, the power conversion efficiency of OIHMHPs has reached up to 22.1%.

This sparked interest in studying additional recently discovered charge storage mechanisms, mainly double layer capacitance and pseudo capacitance, which offer a way to boost energy density and storage. Fast and reversible redox reactions and the electric double layer that hosts charges on the electrode surface are the two ways that pseudo capacitance is produced. The most practical way to boost energy storage density and capacity would be to raise the capacitance per unit area. The equation $C = \epsilon A/d$, where ϵ is the dielectric constant, A is the

electrode area, and d is the thickness of the insulator between the two conductive plates, can be used to increase the double layer capacitance.²

2. Halide Perovskites

A class of materials known as halide perovskites has the general chemical formula ABX_3 , where X is a halide anion such as iodide, bromide, or chloride, B is a metal cation such as lead or tin, and A is a cation such as methylammonium (MA) or cesium (Cs). These substances typically possess three-dimensional (3D) crystal structures. They have been the subject of much research recently because of their remarkable qualities as light absorbers in solar cells. While these materials are effective for this use, efforts are concentrated on making them more stable for use in device applications. In order to develop these materials into other kinds of devices, a lot of research is also being done to examine their properties. The ease of use and low cost of fabrication of perovskite materials makes them appealing for use in a variety of low-cost electronics. Thus far, a significant portion of this work has been devoted to 3D materials. Some, though, are making use of the more recent 2D materials. In particular, the 2D materials and devices derived from these will be the subject of this review. The term AMX_3 , which stands for hybrid organic-inorganic halide perovskites, was initially used in 1850 to refer to minerals that shared the same crystal structure as calcium titanium oxide. Their use in solar cells has garnered a lot of attention in the last ten years, as their maximum power conversion efficiencies have increased from 3.8% to the most recent record of 22.7%. The simplest way to describe them is as 'A' site organic cations and 'B' site inorganic anions arranged in a BX_6 octahedral network. They can also be divided into 2D and 3D structures according to whether or not they contain organic cations. The first significant benefit of 2D perovskites arises from this, which is that the presence of large organic cations between the perovskite layers greatly improves stability and significantly lowers the likelihood of phase transitions. More information on this will be covered in the section on properties. The bandgap's tunability, which enables absorption of a wider range of wavelengths than for 3D perovskites, is another significant benefit. This has been demonstrated by adding 2, 3, or 4 carbon alkyl chain amines to the A site of 2D perovskite to modify its basic structure. However, this process only produces 50% 2D perovskite; the remaining 3 structures are cubic. More recently, PbI_2 and A salts have been annealed in a powdered form inside a tube to create 2D perovskites. Tetraethyllead-based perovskites have also demonstrated potential as a low-cost tin replacement material for thin-film solar cells.^{3,4}

2.1. Properties

Ion conduction: Halide perovskites have good ion conduction qualities in addition to their electrical ones. This facilitates the effective movement of ions within the material, which is essential for energy conversion and storage devices. Perovskites have a high ionic conductivity, which makes them perfect for applications like supercapacitors and batteries because it allows for rapid charging and discharging rates. Perovskites' potential for use in solid-state electrolytes is further increased by their capacity to transport both cations and anions. This is crucial for the advancement of solid-state batteries since they are more stable and safer than conventional liquid electrolyte batteries. For a variety of energy storage and conversion applications, halide perovskites are extremely versatile materials due to their combination of electronic and ion conduction properties.⁵

2.2. Applications

Halide perovskites are used in supercapacitors because of their exceptional ionic and electronic conductivity as well as their capacity to exist in several crystal phases. They are used for energy storage for the first time by Sharma et al. They showed that $CsPbBr_3$ could be successfully utilized as an electrode material by grinding it into the appropriate crystal phase. They contend that adjusting the crystal phase offers a great deal of flexibility in adjusting the electronic characteristics of perovskite electrodes. When cycling $CsPbBr_3$ in an ionic liquid, Yang et al. observed a phase transition. They showed that the fast kinetics of the high phase transition led to a significant increase in capacitance in the high phase, effectively forming a solid solution between the high and low phases. This offers an additional technique for adjusting the electronic characteristics through repeated cycles of the phase transition in the perovskite. As Shi et al. showed with nickel ions, doping can further stabilize the high phase, leading to a high capacitance and long cycle life. Lastly, they demonstrated via first principles calculations that perovskites with A-site vacancies have smaller band gaps and higher conductivities, indicating yet another way to fine-tune electronic properties.⁶

3. Supercapacitors

The two electrodes of an electrochemical double-layer supercapacitor (EDLC) are divided by an electrolyte. An applied voltage causes the Helmholtz double-layer in the right electrode (carbon) to open (Fig. 1), allowing ions to adsorb and store energy. Using an external power source, electrons are transferred between the electrodes during this operation, building up a charge at the second electrode that is opposite in sign and equal in

magnitude to the charge at the first electrode. This energy can be released at a later date in order to discharge the EDLC.

Similar to the ruthenium oxide/titanium oxide-based supercapacitor, pseudo capacitors are made of the same materials as EDLCs, with the exception that a redox reaction occurs at the electrodes, resulting in the bulk or surface of one electrode being used for faradaic charge storage. A conducting polymer or transition metal oxide with a high degree of surface oxidation and electrical conductivity makes up the electrode of a pseudo capacitor. Pseudo capacitor build-up and electrolyte breakdown from the redox reaction result in significantly reduced stability, cyclic life, and rate capabilities, even though pseudo capacitors can achieve higher capacitance values than EDLCs. The faradaic capacitance that results from a redox reaction at the electrode and the capacitance of the double-layer combine to store electrical energy in perovskite supercapacitors.⁷

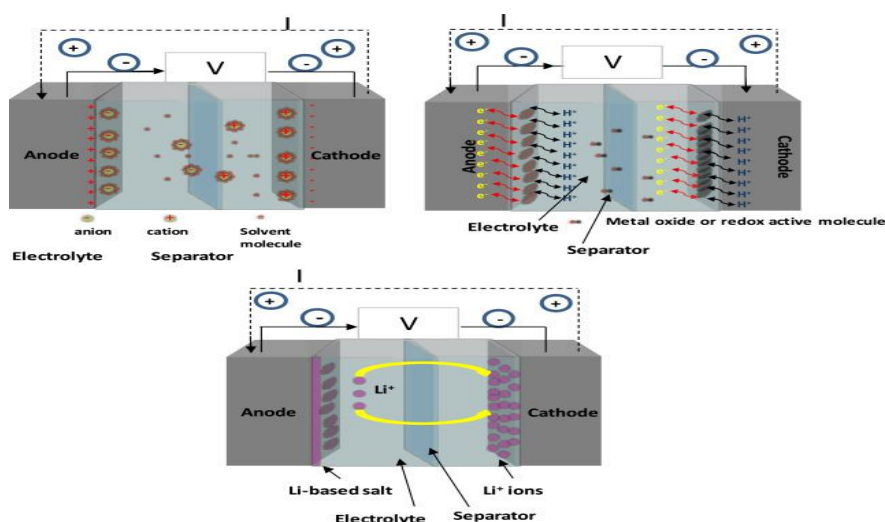


Fig. 1. Schematic representation of (A) an electrical double-layer capacitor (EDLC), (B) a pseudocapacitor, and (C) a hybrid supercapacitor (HSC).

At a high power and energy density, an ideal electric double-layer capacitor would demonstrate long-term charge storage without any energy loss. The degree of ion accumulation determines how much charge is stored, which is directly correlated with the applied voltage. Compared to dielectric capacitors, the device has a larger energy storage capacity, though it might discharge the energy more slowly. After being physically and arbitrarily stored, the energy is released when the voltage source is cut off. Because of this, EDLCs have a long cycle life, high cell voltage, and are highly reversible systems. Ions build up on the surfaces of both electrodes during charging as a result of voltage being applied to one of the electrodes—positively—and the other, negatively. At each electrode, there is a similar process to the Faradaic reaction that involves the transfer of electrons between the electrode and the electrolyte ions that have been adsorbed on the electrode surface. The process is called electrochemical adsorption, and because the ions are confined to the electrode surface, their entropy is decreased as they are solvated to the electrode.

The last ten years have seen a significant increase in interest in supercapacitors as an energy storage technology because of their high-power density, long-term stability, and quick charge time. The interface between the high surface area electrode material and the electrolyte is where supercapacitors, also known as electrochemical capacitors, store energy. Redox reactions or static charge separation in the Helmholtz double layer are the main methods used to accomplish this storage. In the former case, energy is stored electrostatically within a small potential window, whereas in the latter case, faradaic reactions produce pseudo-capacitance. The dominance of double layer storage with low reversibility of faradic reactions is responsible for the supercapacitors' long cycle life, high power density, and duration of energy release. $E = 1/2CV^2$, where C is the capacitance and V is the potential, represents the energy stored in capacitors. When comparing this to battery energy storage, we can see that there is no chemical reaction involved—just the storage of charge. Supercapacitors benefit from faster charging and discharging as well as longer lifespan as a result. In the case of pseudo-capacitance, the energy density is correlated with the specific capacitance of the active material and faradaic charge transfer reactions, whereas in electrostatic storage, it is directly proportional to $1/C$. Andres and colleagues computed a Ragone plot using this data, where the y-axis represents power delivered and the x-axis represents energy. The power characteristics displayed in this plot were ten to a hundred times greater than those of batteries, and supercapacitors had about 10% of the energy in the best batteries.⁸

4. Two-Dimensional Halide Perovskites

By altering the process used to create 3D perovskite, 2D perovskite can be synthesized. The solution method is one of the main ways to synthesize perovskite, and mechanical ball milling is another economical way. The precursor for the 2D perovskite is partially dissolved in a solvent before being added to a different solvent with a low dielectric constant. The anion will create a sheet of perovskite with n layers separated by that anion. Typically, this technique employs acetone or another suitable solvent in addition to DMF or DMSO as the solvent.

Without an X anion, the general formula for layered perovskite is $(A^{2+})_2 B_{(IV)} X_4^{2-}$. If the d 10 metal (such as Pb and Sn) increases its coordination number, the structure can change to a double layer and so on. A spacer cation A separates each of the n layers of perovskite represented by the general formula $A_{2+n-1} A_n B_{(IV)} X_{3n+1}$. Accordingly, $n=1$ for a double layer and $n=2$ for a triple layer. A can be swapped out for other cations because it is a cation. Perovskite that forms in this manner eventually resembles mica structurally. By increasing the number of layers and using an organic spacer cation between each layer, two-dimensional perovskites with a stone and rock salt structure can be simulated. There are no corner-sharing octahedra in the structure of the 2D perovskite since it only has an octahedral framework in the surface direction. One layer ($n=1$), two layers ($n=2$), three layers ($n=3$), and so forth are some examples. When it comes to stability, this type of structure may be superior to 3D perovskite. The primary problem with 3D hybrid perovskite is stability. Perovskite and composite materials have a lot of potential for solar cells because of perovskite's excellent light absorption capabilities.⁹

4.1. Synthesis

Two techniques are available for the synthesis of two-dimensional (2D) perovskites. The most popular technique involves combining the 2D perovskite compound with the 3D post, which will dry up the 2D perovskite residue while the 3D post absorbs the organic moieties from the 2D perovskite specifically. A large range of 2D perovskites, including the $n=1$ Ruddlesden-Popper phases and, more recently, the $n=2$ phases, have been successfully synthesized using this approach. An alternative method for creating 2D perovskites is to mix polar and non-polar solvents. The non-polar nature of the organic moieties in 2D perovskites causes them to preferentially form a compound with the non-polar solvent; when combined with a polar solvent and a co-solvent that is also a 3D perovskite, they form a compound that is also 2D perovskite. Using this second technique, 2D perovskites monolayers have been created by placing the solution on a substrate that interacts more intensely with the polar solvent, resulting in the formation of a monolayer at the top.¹⁰

4.2. Properties

Using differential scanning calorimetry, the phase transition temperature of thin films of $(RNH_3)_2(CH_3NH_3)_{(n-1)}Pb_{(n+1)}I_{3n+1}$, where $R=Cs$, $n=1$, and $n=2$, was measured in order to assess the thermal stability of these materials. It was discovered that the phase transition temperature of each material was approximately 100°C. The band gap in multi-layered 2D perovskites is tuned at approximately 1.65 eV, which is the ideal thickness for absorption by solar cells. This is the hybrid perovskite material's lowest band gap ever discovered. These materials might be appropriate for high-efficiency tandem solar cells with a band gap of 1.65 eV, given their high charge carrier mobility and high absorption coefficient caused by significant photoactivity along the perovskite layer planes. By adjusting the halide and the A-site cations, the band gap and other semiconductor characteristics in bulk 3D perovskites can be tuned. However, it has been demonstrated that the band gap and refractive index in these hybrid 2D perovskites are essentially unaffected by the cation employed. Rather, the primary means of adjusting them is through varying the quantity of inorganic perovskite layers. When the bulk material is reduced to a thin layer, quantum and dielectric confinement effects take place.¹¹

5. Stability Challenges

The degradation of hybrid organic-inorganic perovskite resulting from compositional breakdown in the presence of moisture is the cause of its moisture sensitivity. As a result, solar cells are degrading quickly, and all varieties of perovskites are experiencing stability issues. The breakdown of PbI_2 in its intermediate state in dimethylformamide (DMF) or dimethylsulphoxide (DMSO) and the subsequent reaction with MAI to produce the final product of organometallic perovskites may be the cause of the degradation of $MAPbI_3+MAPI$, which is associated with the structural change. Due to DMSO's high volatility, PbI_2 was able to be converted into $MAPbI_3+MAPI$ during open-air evaporation. This process then led to the formation of thin films through the hot casting method after cooling. Environmental influences have a significant impact on the stability of Pb-Sn and Pb-hybrid perovskites. The degradation of perovskite films has been attributed by the researchers to exposure to UV light and higher temperatures. As is well known, the use of organic cations and heavy metal lead causes instability in perovskites. For organic cations, the general formulas are $Rb+Cs=1$, $FA=CH(NH_2)_2$, and

MA=CH₃NH₃. It has been demonstrated that perovskite is more stable when it contains more Cs and FA than the widely used MAPbI₃. Humidity degradation has decreased because of FA replacing MA. Tin took the place of lead, and this enhanced perovskite's stability and resistance to temperature changes. It was reported that the thin films used to create solar cells remained stable for up to five hours at temperatures as high as 300°C, with PbSnI₂ having the highest efficiency at 14%.

Regarding chemical stability, photoluminescence studies revealed degradation: when exposed to ultraviolet light, organic matter oxidized into carbon dioxide and water, forming black lead oxide. This suggests that because lead (II) is so prevalent in 2D perovskites, they show poor resistance to oxidation and reduction, and it is challenging to shield them from reactions with other materials. Determining the precise type and mechanism of chemical reaction in the perovskite environment is crucial to identify the underlying cause of material instability, as any chemical changes have the potential to modify the material's electrical properties. The hardest problem to solve is environmental stability since it requires such a deep understanding. Perovskites in two dimensions possess a soft mechanical structure that allows for slight external force to cause deformations. Furthermore, in high humidity environments where the chemicals alternate between being solvated with water and being in dry crystal states, they can exhibit structural failure. This may occasionally result in an irreversible phase change and cause structural damage to perovskites.

Heat and moisture will both severely degrade the material's qualities because halide perovskites are inherently hydrophilic. Despite the insulating qualities and 150°C thermal stability of 2D perovskites, the material can still be degraded by oxidation or hydrolysis when heated electrically during processing or operation. To guard against thermal degradation, the voltage over potential window mentioned earlier needs to be raised. After being exposed to different organic solvents for a month, the 2D halide perovskites showed no signs of phase change, indicating their exceptional structural stability. These materials must, however, continue to work in all applications despite being in contact with their surroundings. As a result, there are certain stability issues that must be resolved first. For high temperature applications, it is imperative to accurately characterize the thermal stability of any materials under consideration. Since many functional perovskite oxides are known to act as active catalysts in the partial oxidation or steam reforming of hydrocarbons, these reactions frequently take place at temperatures above the one that is ideal for SOFC operation. Understanding the stability of perovskite and potential material interactions between it and the electrode/cell components is therefore crucial. It has been demonstrated that under relatively mild heating, 2D perovskites melt or break down into their constituent ions. For instance, it has been demonstrated that, when heated to 100°C, the n=1 Ruddlesden-Popper phase n-octyl ammonium lead iodide breaks down into the n=1 phase and free iodine; higher n values cause the organic layer to be lost and the phase to change into the n = 1 phase. This is a blatant sign that using the materials in hot environments is not recommended. It has also been demonstrated that the 2D PEA-based perovskite materials are thermally unstable. The FAPbI₃ and MAPbI₃ powder X-ray diffraction patterns demonstrate that decomposition into PbI₂ and mixed organic/hydrocarbon products happens in just 4 hours at 85°C.¹²

6. Strategies for Enhancing Stability

One study has demonstrated that it might be feasible to increase stability by purposefully introducing a defect in the perovskite structure as opposed to the formation of an insulating layer. The formation of Pb vacancies by the addition of a small amount of foreign metal atoms has been demonstrated by N-chem and Udagawa et al. to decrease the rate of halide ion migration and hydrolysis of the metal halide octahedra.

Creating an insulating shell to enclose the perovskite material and impede ion migration is one method of stopping ion migration and slowing down the rate of degradation. To create a passivated layer on the surface of perovskite solar cells, a thin layer of oxide material is occasionally sputtered on. Using ALD or CVD to deposit an oxide or nitride layer on the perovskite surface is a more controlled way to create an insulating shell. This was recently shown by Daramola and colleagues, who found that the material was significantly more stable in acidic conditions than the unmodified material after using ALD to deposit a layer of Al₂O₃ on a perovskite film. To significantly increase stability, comparable research on perovskite supercapacitor materials could be done.

The creation of composite materials is an alternative strategy in the ongoing effort to increase material stability. In order to create a layered structure that is more stable than the pure perovskite material, the most popular technique in this case is to combine metal halide perovskite materials with other polymers or inorganic materials. The discovery of single-layer two-dimensional perovskites, also known as Ruddlesden-Popper (RP) phases, is an exciting development. These perovskites are created by quenching the reaction of a three-dimensional perovskite and lack a formal inorganic A-site. The inorganic framework of RP phases, as revealed by crystallographic studies, is made up of an infinite sheet of corner-sharing octahedra rather than isolated BX₆ octahedra. By inhibiting the ready hydrolysis of the metal halide octahedra, this offers the potential to significantly increase stability; however, studies on these materials are still in their very early phases.

Since two-dimensional lead halide perovskites are known to degrade due to water infiltration, the high stability of these supercapacitors poses a challenge. Nonetheless, it is widely known from the literature that careful chemical composition selection can regulate the stability of metal halide perovskites. Increasing the inorganic content above what the stoichiometry of the natural ABX_3 perovskite structure requires and/or partially substituting azide or cyanide ions for halide anions are two methods to increase hydrophobicity. Although each of these materials creates a three-dimensional perovskite structure, it's likely that the ideas will apply to two-dimensional perovskite materials as well.¹³

7. Fabrication method

There are many different fabrication processes and strategies available for creating electrodes for use in supercapacitors. Wet-chemical methods, dry film methods, and direct growth methods are the three main categories into which the techniques can be broadly classified. Most of the work involving 2D perovskites has been focused on the wet-chemical methods, which are also popular for forming supercapacitor electrodes, because of the high interest in perovskite-based solar cells and their compatibility with other thin films and substrates. To create a thin film, the perovskite must first be synthesized into a solution that can be spin or drop cast onto a substrate. This approach is straightforward, efficient, and capable of producing well-focused, high-quality films. At temperatures between 70 and 150°C, common solvents include N, N-Dimethylformamide, and Dimethyl Sulfoxide. Doctor Blading is a high throughput method that has been used to form perovskite films in addition to drop and spin casting. As an alternative, the dry film method forms a film by first allowing the solvent to evaporate, leaving the film behind. Due to its ability to prevent perovskite decomposition from solvent exposure, this method has been widely used. The perovskite is synthesized onto the current collector substrate in direct growth methods. One example of this that may have applications in supercapacitors is the direct growth of a uniform, high-quality film onto a substrate through Chemical Vapour Deposition. This technique reduces the amount of post-synthesis processing for the perovskite film.¹⁴

8. Electrochemical performance

The most crucial component of EDLCs is their electrochemical performance, which is dependent on the inherent qualities of the electrode material. The CV curves of the 2D and organic-inorganic perovskites exhibited shapes resembling rectangles, which demonstrated the electrical double layer behaviour. Low charge transfer resistance, especially at the electrode/electrolyte interface, is suggested by the logarithmic plots' straight lines and the 2D perovskite's extremely low $I\&C$ values. The Nyquist plots of both materials, which displayed a clear semicircle in the high-frequency region and a linear region at higher frequencies, corroborated this. The organic-inorganic perovskite's semicircle diameter was considerably greater than the 2D perovskite's, indicating a greater charge transfer resistance at the electrode/electrolyte interface. The real axis was intersected at a frequency of 0 by extrapolating the straight-line regions of both plots. The 2D and organic-inorganic perovskites had $R\backslash C$ values of 0.74 k Ω and 2.96 k Ω , respectively. The Warburg impedance and diffusion coefficient of the ions in the electrolyte are represented by these values, which line up with the gradient of the lines. Higher rates of charging and discharging will follow from faster ion diffusion caused by a lower charge transfer resistance. A non-uniform pseudo-capacitive response was suggested by the organic-inorganic perovskite Nyquist plot's constant slope from the high to low frequency region. The CV plot, which showed how the curves were not rectangular, provided additional evidence for this. Research on 2D perovskite in conventional supercapacitors and its kinetic states in the new phase of matter, covering both the pseudo-capacitive and electric double layer aspects, will be especially interesting going forward.¹⁵

9. Structural Characterization

X-ray diffraction (XRD) and infrared (IR) spectroscopy are commonly used to characterize the structure of 2D perovskite supercapacitors. The perovskites' XRD patterns show the crystallites' precise structure, homogeneity, and phase purity. Since 2D perovskites are known to have greater rotational freedom around the organic cation, it may be more challenging to figure out their structures. Our group is currently using XRD and neutron diffraction, two techniques used in the Rietveld refinement of perovskite structure, to determine the detailed structures of the perovskite layers. This technique allows for the comparison of the effects of organic and halide cations on the perovskite structures and provides detailed information about atom positions. In addition to providing details on molecular vibrations and lattice parameters, IR spectroscopy can be used to track any structural alterations in the perovskites. It is also possible to observe the surface of the perovskites and any alterations in the microstructure brought about by the supercapacitor tests using high-resolution transmission electron microscopy (HRTEM). The various perovskite phases can be linked to the lattice fringes, and this technique will yield comprehensive structural information. All of these structural techniques may help to explain

why 2D perovskites are more stable than 3D ones and how this affects the supercapacitor performance of these materials.¹⁶

10. Energy Storage Applications

Energy storage fields have shown a great deal of interest in two-dimensional (2D) materials because of their unique electronic structures. Recently, 2D perovskites—which form as a single unit cell thickness—have been investigated as potential electrode materials for supercapacitors. Low-dimensional organic-inorganic hybrid perovskites were first reported by Cao et al. in 1998. The preparation of the 2D $(C_6H_5C_2H_4NH_3)_2PbI_4$ compound involved the intercalation of butylamine into the 3D precursor. With conducting organic and inorganic layers alternately stacked, it has a naturally occurring quantum-well structure. UV photoelectron spectroscopy yielded an optical energy gap of 2.37 eV, larger than the bulk counterpart. This technique made it possible to decrease the dimensionality of perovskite materials chemically. 2D perovskite materials with a variety of organic and metal cations have been created using this chemical process. The compound $(C_4H_9NH_3)_2PbX_4$ (X= Cl, Br, I) and its related compounds have been thoroughly studied by Yamada's group. The single-layer perovskites were successfully separated from the bulk compound, and the quantum size effect was clearly visible on the optical spectra. Large dielectric constants were found in the electrical field over a broad frequency range, with the lowest frequency showing the maximum, indicating that the carriers were concentrated close to the band gap. These special qualities, which arise from the electronic state's confinement in a two-dimensional plane, are anticipated to find use in optoelectronic and electronic devices.¹⁷

Supercapacitor Performance-

R. Kumar and M. Bag 2022¹⁸ stated that over the past ten years, hybrid halide perovskites—a mixed electronic-ionic material—have gained a lot of popularity because of their numerous applications in flexible optoelectronics, particularly in energy conversion and light-emitting devices. Although the primary reason for the instability of these materials' devices in hot and light conditions is ion migration, this characteristic can also make them perfect for energy storage applications like Li-ion batteries, photo rechargeable batteries, and supercapacitors. This article summarizes the current state of research on electrochemical supercapacitors based on perovskite materials, elucidating the mechanisms of charge storage in these devices and offering significant insights for their future development. Because of ion migration within the bulk perovskite film, these materials' total charge/energy storage can be modulated by the induced field. An essential component of the charge storage mechanism in perovskite-based energy storage devices is the electronic-ionic coupling found in metal halide perovskite materials.

Kumar R, et al 2022¹⁹ stated that the storage of energy and the processing of energy are two distinct aspects of modern off-grid power solutions. We were able to design a photoelectrochemical energy storage system that combines energy harvesting and storage by optimising electrical and ionic conductivity in conjunction with a semiconductor that is capable of absorbing light across the solar spectrum. This allowed us to harvest energy and store it. Here, we provide information about one such device, which is a photo rechargeable supercapacitor that is based on halide perovskite. Through the utilisation of its high-power density of 1875 W kg⁻¹ and its energy density of 30.71 W h kg⁻¹, this gadget is capable of being charged. We present a method for fabricating efficient photo rechargeable supercapacitors by utilising the semiconducting and ionic properties of halide perovskites. This method achieves a photocharging conversion efficiency (η) of approximately 0.02% and a photoenergy density of approximately 160 mW h kg⁻¹ when the supercapacitors are exposed to a white light source of 20 mW cm⁻². The high absorption coefficient, long carrier diffusion length, and strong ionic conductivity of halide perovskites are some of the characteristics that describe these materials. The production of photorechargeable supercapacitors with better electrical conductivity is accomplished by enhancing porous perovskite electrodes with carbon black. In addition, we present a comprehensive study of the photoelectrode, which is intended to promote an understanding of the fundamentals, stability, limitations, and potential future applications of photorechargeable supercapacitors that are based on halide perovskites.

Sandhu A and Chini M.K. 2024²⁰ stated that MHPs, or metal halide perovskites, are very promising materials for use in energy storage systems. Two-dimensional (2D) halide perovskites are gaining significant attention for use in supercapacitors due to their intriguing characteristics, which include electronic confinement, structural flexibility, attractive performance, and stability. However, one of the most promising materials for supercapacitors is three-dimensional (3D) halide perovskites because of their low exciton binding energy and long-range carrier transport nature. For effective energy storage devices, these materials have emerged as one of the most promising mixed electronic-ionic materials. The physicochemical and electrochemical properties of 2D and 3D MHPs are different, and they can form hetero-structures to improve their electrochemical properties.

Understanding MHPs' synthesis, characteristics, and numerous electrochemical facets as well as their supercapacitive behaviors is crucial.

Rao M.K., et al. 2023²¹ stated that the most extensively studied materials in the field of photovoltaics are hybrid halide perovskites. Due to their special conductivity, they have recently been studied for energy storage applications. The majority of studies on halide perovskites' use in supercapacitors rely on compounds called methyl ammonium lead iodide (MAPbI₃) and methyl ammonium lead bromide (MAPbBr₃). The external environmental parameters can cause these halides to degrade more easily. In this case, quasi 2D perovskites—which combine the qualities of both 3D and 2D perovskites—can produce notable results with improved stability. a maximum specific capacitance determined by cyclic voltage curves of 8.67 F g⁻¹.

Future Prospects

In addition to its easy deposition and solution synthesis, 2D perovskite exhibits good device performance, making it a very promising material for devices in the future. Supercapacitor devices are very sensitive to moisture and water because of the ionic transport involved. In addition to enhancing the device's overall performance, such as raising the potential difference and energy density, we are also interested in extending the device's lifetime and stability against these elements. Swapping out the present organic cations for a bigger inorganic cation, like Cs⁺, is one way to potentially solve this issue. It will be more effective at preventing moisture from entering the device and will reduce water vulnerability because it will offer more structural stability and the cation is less polar. The slow charge/discharge process is another problem that needs to be fixed. Even though the ion mobility in perovskite is relatively high, the easily extracted ion is only found at the surface, and because of the bulk's crystalline barrier and electron-hole localization, it is difficult to extract the ion. However, we think that by creating a better ion electrode with a material that has good reversible ion adsorption, we might be able to solve this issue. Finally, we would like to create a flexible supercapacitor device that can be used with portable and small electronics. We think it might be possible to use the 2D perovskite to create a flexible supercapacitor device because the perovskite material is notable for its flexibility in some situations. This is probably going to usher in a new era of supercapacitor devices based on perovskites.

Conclusion

In summary, we offer five potential avenues for future research in this area, all from the standpoint of reliability: (i) Research on systematic stability. To promote the stability of 2D perovskites, it is more important to understand their intrinsic degradation effect rather than concentrating on their efficiency and electronic properties. In order to assess the long-term durability of 2D perovskites, studies on their thermal and environmental stability are essential but incomplete. A standard stability test must be carried out while taking into account the typical lifespan of the relevant devices. To quickly assess the stability of perovskites, accelerated aging tests will also be created. (ii) Material identities materializing for increased stability. To achieve stable 2D perovskites with the desired photoelectric or optoelectronic properties, one must grasp the structure-property relation. There is still a lack of knowledge regarding the function of A-site cations or their interaction with the intermediate PbI₂ layer in 2D perovskites. The primary causes of intrinsic Pb-based perovskites' instability in damp or lit environments are their ionic mobility and unfavourable interactions with oxygen or water. The stability of perovskites can be significantly altered by slight modifications to the crystallographic or chemical structure, such as through alloying or crystal phase engineering. (iii) Determining stability standards. To compare and assess the stability of various 2D perovskites, a general stability criterion must be established due to the diversity of 2D perovskites in terms of their structures and properties. In order to take preventative action, a phase diagram or guideline that highlights the dangerous circumstances for 2D perovskites can be created. (iv) Defect passivation strategies. 2D perovskites may have flaws that act as points of degradation. Numerous tactics have been shown to be successful in increasing the stability of 3D perovskites, and comparable research will be carried out on 2D perovskites. These tactics include the addition of large organic cations and the introduction of pre-synthesized nanoparticles to passivate the defects. (v) Stable 2D perovskites cannot be used in electronic devices until the material has been shown to be stable. The success of 3D perovskites may still be attributed to the stability of 2D perovskites, despite the great potential of 2D perovskites to replace stable devices like perovskite solar cells.

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