Zero-Dimensional Methylammonium Bismuth Iodide-Based Lead-Free Perovskite Capacitor

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ABSTRACT: Symmetrical electrochemical capacitors are attracting immense attention because of their fast charging–discharging ability, high energy density, and low cost of production. The current research in this area is mainly focused on exploring novel low-cost electrode materials with higher energy and power densities. In the present work, we fabricated an electrochemical double-layer capacitor using methylammonium bismuth iodide (CH$_3$NH$_3$)$_2$Bi$_2$I$_9$, a lead-free, zero-dimensional hybrid perovskite material. A maximum areal capacitance of 5.5 mF/cm$^2$ was obtained, and the device retained 84.8% of its initial maximum capacitance even after 10 000 charge–discharge cycles. Impedance spectroscopy measurements revealed that the active layer provides a high surface area for the electrolyte to access. As a result, the charge transport resistance is reasonably low, which is advantageous for delivering excellent performance.

INTRODUCTION

Organic–inorganic halide perovskite materials captured the attention of the scientific community during the past few years because of their unique optical and electronic properties. Three-dimensional hybrid perovskites with a general formula of AMX$_3$ (A = methylammonium or formamidinium cation; M = Pb$^{2+}$, Sn$^{2+}$, etc., and X = I, Br, and Cl) are highlighted as efficient light-absorbing layers in solar cells with an efficiency surpassing 22%. Apart from photovoltaic applications, these materials are promising for light-emitting diodes, photodetectors, sensors, memories, and so forth. The widespread applications of this class of materials could be attributed to their properties such as tunable band gap, large absorption coefficient, high electron and hole diffusion lengths, good charge carrier mobility, ease of defect state formation, and excellent ion migration. Even though hybrid perovskites exhibit very interesting properties and are useful for a large number of applications, the toxicity of lead and instability in the presence of moisture and oxygen are prime concerns preventing their commercialization.

Storage of energy is as important as its production. Development of novel, environmentally friendly, and sustainable energy storage devices has attracted considerable research attention in modern times because of the rapid depletion of unsustainable fossil fuels and environmental deterioration, which are also necessary to satisfy the demands of the fast-growing electronic industry. Electrochemical capacitors with long life span, high power density, and fast charge–discharge characteristics are regarded as excellent energy storage devices, as they have the potential to complement or even replace batteries in numerous applications. However, their low energy density is a limiting factor in their widespread practical applications. Hence, the current research in electrochemical capacitors is mainly focused on exploring novel low-cost electrode materials with higher energy and power densities. In this context, hybrid perovskite materials are promising because of their high ionic conductivity; a recent study suggests that the ionic conductivity of methylammonium lead iodide (MAPbI$_3$) is higher than its electronic conductivity. By exploring this property, Zhao et al. have reported a MAPbI$_3$-based thin-film electrochemical double-layer capacitor (EDLC). The capacitance obtained was 5.89 mF/cm$^2$, which proved that hybrid perovskite materials are good candidates for capacitor applications. However, the toxicity of lead is a major factor of concern here also.

RESULTS AND DISCUSSION

In this work, we have explored the potential of methylammonium bismuth iodide (MBI), which is a lead-free, zero-dimensional perovskite having a unit cell formula of (CH$_3$NH$_3$)$_2$Bi$_2$I$_9$, for energy storage applications. This bismuth-based perovskite is an environment-friendly alternative with better atmospheric stability than that of the corresponding lead-based perovskites. The unit cell of MBI consists of isolated...
Bi$_2$I$_9$$^-$ units surrounded by methylammonium cations (Figure 1a). Bi$_2$I$_9$$^-$ is formed through face sharing of two BiI$_6$$^-$ octahedra. We have hypothesized that the isolated Bi$_2$I$_9$$^-$ bioctahedra can supply vacant spaces and large surface area so that the electrolyte can easily access the active material, resulting in enhanced ionic charge transport. This would lead to capacitors having high energy density. To prove this, we have fabricated capacitor devices with the MBI material and analyzed them using cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) techniques. The charge transport resistance obtained from the impedance measurement was small, which was in agreement with the large surface area provided by the material.

(CH$_3$NH$_3$)$_3$Bi$_2$I$_9$ was characterized using transmission electron microscopy (TEM), ultraviolet–visible (UV–vis) absorption, and X-ray diffraction (XRD) spectroscopy. The TEM image of MBI is shown in Figure 1b which indicates that the material forms a thin film of interconnected MBI crystals. The high-resolution transmission electron microscopy (HRTEM) image of the material is shown in Figure 1c, and the corresponding electron diffraction pattern is shown in the inset. The diffraction pattern shows lattice distances of 3.51, 3.62, and 3.74 Å corresponding to the (202), (006), and (105) lattice planes, respectively. Clear visibility of the lattice planes and the hexagonal array of bright spots indicate that the material is highly crystalline. MBI exhibited a broad absorption ranging from 300 to 600 nm in the UV–vis absorption spectrum (Figure 1d). The optical band gap of MBI calculated from the onset of the absorption was 2.22 eV. XRD patterns obtained from powdered samples, which are in good agreement with the previous reports, revealed the hexagonal crystal structure of the material, with the characteristic perovskite doublet peak at 2$\theta$ = ~12$^\circ$ (Figure 1e). The XRD profile of the material was studied over a period of 1 month (Figure S1, Supporting Information). No variation in peak position or intensity was observed, which indicated the good stability of the material under ambient conditions.

For analyzing the electrochemical energy storage performance of the material, MBI was coated on a carbon cloth substrate having an area of 1 cm$^2$, which was used as the electrode. A polymer separator soaked in an electrolytic solution (30 mg/mL methylammonium iodide in butanol) was sandwiched between the MBI-containing electrodes to form a symmetric capacitor. Additives (5 wt %) such as polytetrafluoroethylene (PTFE) and activated carbon were added during the preparation of the electrode for proper binding of the perovskite material on to the carbon substrate and for improving the conductivity of the active layer. A simplified schematic representation of the device is shown in Figure 2a. The thickness of the active film was about 400 nm as measured from the cross-sectional scanning electron microscopy (SEM) image which is shown in Figure 2b. The perovskite material was uniformly coated over the carbon cloth substrate, as shown in the topological SEM image (Figure 2c). The root-mean-square roughness of the film obtained from the atomic force microscopy (AFM) height image (Figure 2d) was 16.7 nm, which means that the surface roughness of the film was reasonably high. Such a high surface roughness is good for energy storage applications because the electrolyte can strongly interact with the active layer. The high surface roughness of the film is in good agreement with the topological SEM image, which showed relatively large MBI crystals (Figure 2c).

The symmetric EDLC assembly was then sandwiched in a standard electrochemical cell (ECC-std, EL-CELL GmbH), and the capacitive performance was evaluated by CV, galvanostatic charge–discharge, and EIS techniques. The CV loops did not show any peaks during forward and reverse scans which indicates that the electrodes are charged and discharged at a constant rate during a complete voltammetric cycle (Figure 3a). It is clearly found that the areal capacitance value was

Figure 1. (a) Unit cell representation of MBI. (b) TEM image of the MBI film. (c) HRTEM image of MBI, with a fast Fourier transform image in the inset. (d) Absorption spectra of MBI in the film state. (e) Powder XRD of MBI.
decreasing with an increase in applied scan rate or current density (Figure S2, Supporting Information). This property implies the EDLC behavior of the device, which means that at lower scan rates, ions are getting enough time to occupy the vacant spaces supplied by the MBI perovskite film and at higher scan rates, the charge accumulation happens only at the electrode surface.

The galvanostatic charge−discharge curve was symmetrical, which is a characteristic of an ideal EDLC behavior (Figure 3b). The results obtained from the charge−discharge measurements were in good agreement with those from CV measurements, indicating that no surface redox reactions are happening in the device in the given voltage range. The long-term cycling stability of the capacitor device was evaluated from repetitive galvanostatic charge−discharge measurements for 10,000 cycles at a current density of 2 mA cm$^{-2}$. The capacitor retained 84.8% capacitance of its initial value even after 10,000 cycles (Figure 3c). The Nyquist plot and the equivalent circuit diagram are shown in Figure 3d. In the equivalent circuit diagram, the electrolyte solution resistance ($R_s$) was connected in series to the double-layer capacitance ($C_{DL}$). $R_{CT}$ is the charge-transfer resistance of the electroactive material, and $Z_W$ is the Warburg impedance associated with ion diffusion in the electrolyte. The charge-transfer resistance ($R_{CT}$) of the electroactive perovskite material was calculated from the diameter of the semicircle in the higher frequency range of the Nyquist plot and was found to be 50 Ω. The X-intercept of the semicircle arc in the Nyquist plot gives the value of $R_s$, which is also known as the equivalent series resistance. The lower $R_s$ value (21 Ω) is due to the large electrolyte-accessible surface area provided by the zero-dimensional MBI. This implies that during the charging process, MA$^+$ and I$^-$ ions from the electrolyte can easily access the active perovskite material and in the discharge process, these ions move toward the electrolyte. The straight line in the low-frequency region of the Nyquist plot making an angle of 45° with the X-axis represents the Warburg impedance associated with the ion diffusion in the electrolyte. On the other hand, during the discharging process, MA$^+$ and I$^-$ ions accumulated at the perovskite/electrolyte interface move toward the electrolyte. Because the Bi$_2$I$_9$ octahedra are rigid, the ionic contribution from the perovskite layer will be negligibly small, and thus the perovskite layer acts as an electrode.

The MAPbI$_3$ perovskite-based electrochemical capacitor reported by Zhao et al. exhibited a capacitance of 5.89 μF/cm$^2$. On the other hand, our material has a capacitance of 5.5 mF/cm$^2$, which is almost 1000 times higher than that of the above-mentioned material. It should also be noted that the toxicity and moisture instability of MAPbI$_3$ may prevent its practical applications. The lead-free Bi-based hybrid perovskite...
used in the present work was stable for several months under ambient conditions. The performance of the capacitor devices can be further enhanced by engineering the perovskite material by varying metal ions, organic cations, and electrolytes in addition to the device architecture.

■ CONCLUSIONS
In summary, for the first time, we have fabricated a lead-free perovskite-based symmetric EDLC. A maximum areal capacitance of 5.5 mF/cm² at a scan rate of 5 mV/s was obtained. According to our knowledge, this is the highest value of capacitance reported so far for a hybrid perovskite-based EDLC. Moreover, our findings confirmed that MBI perovskite is an excellent material for EDLC applications.

■ EXPERIMENTAL SECTION

Chemicals. Bismuth(III) iodide (99.9%, Sigma-Aldrich), methylammonium iodide (98%, TCI Chemicals), and N,N-dimethyl formamide (99.8%, Sigma-Aldrich) were used without any further purification.

Synthesis of a Powder (CH₃NH₃)₃Bi₂I₉ (MBI) Material. Bismuth(III) iodide (0.9729 g) (1.649 mM, 1 equiv) and 0.3934 g of methylammonium iodide (2.474 mM, 1.5 equiv) were dissolved in 1 mL of dimethylformamide (DMF) and heated at 70 °C on a hot plate with constant stirring overnight for complete dissolution. The solution was transferred into a Petri dish and heated to 100 °C for about 4 h for the complete removal of DMF. The obtained powder perovskite material was used for further studies.

Characterization. Electronic absorption spectra were recorded on a Shimadzu UV-2600 UV–vis spectrophotometer. For the measurement, the powder perovskite material was kept in between two transparent quartz plates and measured in the reflectance mode. Using Kubelka–Munk function, the reflectance spectra were converted into absorption spectra. XRD studies were carried out on the powder samples with Xeuss simultaneous 2D WAXS/SAXS using Cu Kα radiation (λ = 1.5418 Å). The topological and cross-sectional SEM imaging of the device was performed by subjecting the device to thin gold coating using a JEOL JFC-1200. Characterization. The topological and cross-sectional SEM imaging of the device was performed by subjecting the device to thin gold coating using a JEOL JFC-1200.

Electrochemical Measurements. The electrochemical properties of the capacitor electrodes were studied by symmetric assemblies of the material in a two-electrode configuration by CV, galvanostatic charge–discharge, and EIS using a VMP3 BioLogic electrochemical workstation. The two-electrode configuration is preferred as it provides the most reliable results of the performance of a material for electrochemical capacitors. The cell capacitance (C in F) was then calculated from the CV curves according to eq 1 or from the charge–discharge curves according to eq 2

\[ C = \frac{i}{s} \]  

where “i” is the average cathodic current of the CV loop and “s” is the scan rate.

\[ C = \frac{I}{(\Delta V/\Delta t)} \]  

where “I” is the constant current for charge–discharge and ∆V/ ∆t is the slope of the discharge curve. The areal capacitance \( C_\text{areal} \) (F/cm²) was then calculated as

\[ C_\text{areal} = \frac{2C}{A} \]  

where “A” is the area of each electrode.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00973.

Stability studies of \((\text{CH₃NH₃})₃\text{Bi₂I₉}\) and graphical data representing the variation of areal capacitance with scan rate and areal current density (PDF)

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Notes
The authors declare no competing financial interest.

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