Evolution Characteristics of Perovskite Solar Cells in Air and Vacuum Environments

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Evolution characteristics of perovskite solar cells in air and vacuum environments

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Abstract:
Solid state hybrid organometal halide perovskite solar cells have become the research hotspots recently. We prepared perovskite solar cells by the simple two-step method in the ambient condition. The solar cell samples were kept in air and vacuum environments, respectively. $J_{sc}$ shows good stability in vacuum for up to 27 days, while it drops a lot in air. There is a remarkable promotion of FF for the air-stored samples compared that of the vacuum-stored samples. Changes in $V_{oc}$ of vacuum-stored and air-stored samples exhibited a similar behavior, both showing a slight increase. We believe the moisture in air makes perovskite decompose which leads to the decrease of $J_{sc}$, and the HTM material can be oxidized in air and its conductivity will be improved, which is beneficial to the FF.

Keywords:
Perovskite solar cells, Evolution, Ambient atmosphere, Vacuum

1. Introduction

The methylammonium lead halide (CH$_3$NH$_3$PbX$_3$, X = halogen; CH$_3$NH$_3$: MA) based perovskite solar cells stand out from many new solar cells in recent years, and attract the attention of many scientific researchers$^{1-6}$. Since the proposal of being a light sensitizer for photovoltaic cells by Miyasaka et al. in 2009$^7$, the power conversation efficiency (PCE) record exceeds 20% for the perovskite solar cells recently$^{8,9}$. Compared to other solar cells, perovskite solar cells shows several appealing features, including intense light absorption, excellent ambipolar charge mobility, small binding energy, high efficiency, and low fabrication cost$^{10,11}$.

The PCE of perovskite reached a good level even compared with the traditional solar cells, but the stability of perovskite is poor, especially contact with moisture in air. So besides the pursuit of high PCE, it is also important to know the evolution characteristics of the perovskite solar cells and improve its stability. There are some research on stability of perovskite solar cells with unique structure or composition. With the optimized thickness of the mesoporous TiO$_2$ layer, the PCE can be maintained over

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85% of the initial value after 100 days for the perovskite solar cells stored in air condition\textsuperscript{10}. By introducing an efficient pristine hole-transporting material (HTM), tetrathiafulvalene derivative without the use of tert-butylpyridine and lithium salts, the stability of the dopant-free perovskite solar cells was greatly improved two fold in air \textsuperscript{11}. Baohua Wang \textit{et al.} prepared perovskite films by a modified chemical vapor transport approach, and the perovskite solar cells showed a stable characteristics for 100 days in air \textsuperscript{12}. The relative stability under the same conditions in air also can be greatly improved by using optimal mixed-halide compositions \textsuperscript{13}.

Structure of the solar cells, dopant for HTM, preparation method, and halogen composition are found to be important for the stability of perovskite solar cells, but in all of the previous studies, effects of the atmosphere cannot be ignored. However, the role played by the atmospheric environment on the evolution of perovskite solar cells has rarely been reported. Here we fabricated perovskite solar cells with the simple two-step deposition technique in the ambient condition \textsuperscript{14-17}. To study the role played by the atmosphere environment on the perovskite solar cells evolution, the prepared samples were stored in air and vacuum for several days, respectively. The current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and PCE under different conditions were recorded, compared, and discussed.

2. \textit{Experimental section}

2.1 Materials

All materials were purchased from Sigma-Aldrich, unless otherwise specified, and they were used as received. Methylammonium iodide (CH$_3$NH$_3$I), Co(III) TFSI Salt, and Spiro-MeOTAD were purchased from Luminescence Technology.

2.2 Fabrication of perovskite solar cells

Here, the solar cells were fabricated using the widely used two-step method. FTO-coated glass substrates were cut in the dimensions of 1 $\times$ 1 inch. The surrounding conductive layer was patterned by lithography, then etched using zinc powder and hydrochloric acid followed by diluted hydrofluoric acid, to prevent the leakage on the side. Then the FTO substrate was sequentially washed with acetone, isopropanol, Potassium hydroxide in an ultrasonic bath for 10 min respectively, rinsed with distilled water and dried by nitrogen finally. A compact thin layer of TiO$_2$ was then deposited by RF plasma sputtering using a TiO$_2$-x target. After sputtering, the samples were annealed at 350 $^\circ$C for 1 h in air. Subsequently, a mesoporous TiO$_2$ layer composed of 30-nm-sized particles was deposited by spin coating for 20 s using a commercial TiO$_2$ paste (Dyesol 30 NR-D) diluted in ethanol (2:7, weight ratio). After drying at 120 $^\circ$C for 5 min, the TiO$_2$ films were gradually heated to 500 $^\circ$C, annealed at this temperature for 30 min and cooled to room temperature. Prior to their use, the films were again dried at 500 $^\circ$C for 30 min.

PbI$_2$ was dissolved in N,N-dimethylformamide at a concentration of 462 mg/ml
(~1M) under stirring at 70 °C. The solution was kept at 70 °C during the whole procedure. The mesoporous TiO₂ films were then infiltrated with PbI₂ by spin coating for 40 s. Samples were dried at 40 °C for 5 min and 110 °C for 5 min, respectively. After cooling to room temperature, a solution of CH₃NH₃I in isopropanol (8 mg/ml) was dropped on the films and held for 40 s, making the sample's color turn from yellow to black, then deposited by was spin coating for 20 s, and dried at 110 °C for 5 min.

The HTM was then deposited by spin coating for 30 s. The spin coating formulation was prepared by mixing solution of 72.3 mg Spiro-MeOTAD in 1 ml chlorobenzene, 28.8 µl 4-tert-butylpyridine, and 17.5 µl solution of TFSI in acetonitrile (520 mg/ml).

Finally, 80 nm of gold was thermally evaporated on top of the device to form the back contact. The unit devices have an active size as defined by the size of both the gold and FTO electrodes. The device fabrication was carried out under ambient conditions and a humidity of 25%.

To study the evolution characteristics of perovskite solar cells, we kept samples in two different conditions. A set of samples were stored in normal atmosphere, while the other set of samples was stored in the vacuum condition established by a turbo pump. The vacuum level is about 10⁻⁶ Torr.

![Figure 1. Cross-sectional structure of the device.](image)

2.3 Characterizations

X-ray diffraction (XRD) analysis was performed to investigate the phases of the samples, using a SIEMENS D500. For the Scanning Electron Microscopy (SEM) measurements a FEI Helios Nanolab 660 dual beam was used. J-V characteristic curves were recorded under ambient conditions by applying an external potential bias to the cell while recording the generated photocurrent with an Agilent 4155B source meter. Illumination of the samples was made with a standard ScienceTech SS150 Solar Simulator. The ScienceTech SS150 solar simulator was calibrated to the AM1.5G standard with a standard light meter.

3. Results and discussion
3.1 SEM

Figure 2. Cross-sectional SEM image of the perovskite film synthesized by the conventional two-step deposition method.

The device structure is shown in Fig. 1 (starting from the bottom: glass/FTO substrate, compact TiO₂ layer, mesoporous TiO₂ layer infiltrated with the perovskite nanocrystals, and hole transport layer, with a final Au electrode deposited via thermal evaporation). The results reveal that the perovskite film is uniform despite some pinholes. The cross-section SEM image shown in Fig. 2 shows a well-defined layer-by-layer structure with obvious interfaces. The thicknesses of the compact TiO₂, perovskite, and HTM layers are 60, 310, and 220 nm, respectively. As reported before, the thickness of perovskite layer around 310 nm is optimal and sufficient to serve as the light-absorbing layer ¹⁷, ¹⁸.

3.2 XRD

Figure 3. XRD spectra of Meso-CH₃NH₃PbI₃/Compact TiO₂/FTO.

The XRD pattern of Meso-CH₃NH₃PbI₃/Compact TiO₂/FTO is shown in Fig. 3. The main diffraction peaks centred at 14.2° (110) and 28.5° (220) can be assigned to the CH₃NH₃PbI₃ phase, showing a crystal structure, and the peak centred at 12.7° is attributed to PbI₂ ¹⁰. We observe unreacted PbI₂ remained, which means the conversion of PbI₂ to perovskite on exposure to the MAI solution is incomplete. This incomplete
conversion will affect the final performance of the perovskite solar cells, and more research should be carried out to solve it.

3.3 Evolution of the perovskite solar cells

The evolution characteristics measurements reveal that the vacuum plays an important role in the stability of the perovskite solar cells compared to the samples in air. In order to compare the evolution characteristics intuitively, we normalized all the values with setting the initial value as 1, as shown in Fig. 4.

Figure 4. Evolution of perovskite solar cells stored in air and vacuum, respectively. $J_{sc}$, $V_{oc}$, FF, and PCE are normalized.

$J_{sc}$

Contrary to the air-stored samples without encapsulation, the $J_{sc}$ of vacuum-stored samples is remarkably stable. The $J_{sc}$ of air-stored samples continues to decrease for the 34 days showing significant reduction, while the $J_{sc}$ of vacuum-stored samples remains the same level. As reported by Kim et al.\textsuperscript{19}, the $J_{sc}$ decreases to 85% of the initial value for 8 days, where the devices are stored in air at room temperature. For our samples stored in air, there is only 68% of the initial value after 8 days for the $J_{sc}$, which shows a faster attenuation characteristics. For the vacuum-stored samples, the keeps constant and even rise a little after 25 days.

As well known, the light absorbing layer is the most important factor affecting the photocurrent for the solar cells. Many studies have demonstrated that the MAPbI$_3$ perovskite material is easily decomposed into MAI and PbI$_2$ in the humid environment due to the hygroscopic amine component in the compound\textsuperscript{20-22}. This reveals that the degradation of $J_{sc}$ was mainly due to the decomposition of MAPbI$_3$, as a result of
reaction with H₂O.

\( V_{oc} \)

For both of the samples in air and vacuum, the \( V_{oc} \) shows a jump during the first 5 days. The \( V_{oc} \) of vacuum-stored samples attains a plateau after the jump, while the \( V_{oc} \) of air-stored samples shows a slightly drop and then becomes stable. The \( V_{oc} \) of air-stored samples has a larger rise compared with that of the vacuum-stored samples, and keeps a slightly larger stable value finally. Baohua Wang et al. also found the substantial increase of \( V_{oc} \) with storing the perovskite film for up to 30 days in ambient condition.

After the initial non-stable period, both of the \( V_{oc} \) of vacuum-stored and air-stored samples stabilized and became convergence, and the difference of \( V_{oc} \) is very small after 20 days. This performance shows that air or vacuum environment has little effect on the evolution of the \( V_{oc} \), which means the \( V_{oc} \) of perovskite solar cells is stable under different conditions.

\( FF \)

The FF depends on the series resistance (\( R_s \)), which originates particularly from the charge transport properties of the HTM. As reported by Wang et al. oxidized Spiro-MeOTAD can improve the conductivity of the HTM layer, and enhance the charge transfer at the Au/Spiro-MeOTAD interface. These observations indicate that the oxidation is advantageous for improving the FF, and exposure to oxygen is a critical factor influencing solar cell performance.

During our experiments, FF of air-stored samples increased a lot for the first six days, which can be attributed to the conductivity improvement of the HTM layer caused by the oxidation of Spiro-MeOTAD. It needs 6 days to reach the maximum because the oxidation of spiro-MeOTAD is a dynamic and time-consuming process. Some oxygen exists in the vacuum chamber inevitably, so there is also a rise for the FF of vacuum-stored samples. Due to the lack of oxygen, the improvement of FF is much smaller compared to that in air.

\( PCE \)

PCE is determined by \( J_{sc} \), \( V_{oc} \), and FF with the equation \( PCE = J_{sc} \cdot V_{oc} \cdot FF \). For the first 5 days, the PCE of air-stored samples has a great jump, which is similar as the performances reported by Liu et al. They observed a significant increase of PCE for the first 2 days, and the maximum value was maintained for 3 days at least before it begin to decline. This dramatic increase of PCE benefit from the improvement of FF. The PCE of vacuum-stored samples has the same trend at this rising stage, but it is slower and more modest with respect to the air-stored samples.

After the initial rising stage, PCE of air-stored samples begin to fall and continues, while the PCE of vacuum-stored samples maintain a certain level substantially. This phenomenon is due to the decomposition of perovskite material when contacts moisture.
Actually, we find all the performance parameters of vacuum-stored samples change more slowly than that of the air-stored samples. With more oxygen and moisture in air, on the one hand it is good for the oxidation of HTM, which reduces the $R_s$ and improves the FF, but on the other hand the moisture in air is deadly for the perovskite material which lead to the decrease of $J_{sc}$.

3.4 Best performance of the perovskite solar cells

![Graph showing J-V curves and performance parameters]

**Figure 5.** J-V curves corresponding to the best $J_{sc}$, PCE, $V_{oc}$, and FF.

<table>
<thead>
<tr>
<th></th>
<th>PCE (%)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best $J_{sc}$</td>
<td>10.2</td>
<td>19.2</td>
<td>0.94</td>
<td>0.57</td>
</tr>
<tr>
<td>Best $V_{oc}$</td>
<td>7.78</td>
<td>18.0</td>
<td>1.0</td>
<td>0.43</td>
</tr>
<tr>
<td>Best FF</td>
<td>3.89</td>
<td>8.0</td>
<td>0.75</td>
<td>0.65</td>
</tr>
<tr>
<td>Best PCE</td>
<td>10.2</td>
<td>19.2</td>
<td>0.94</td>
<td>0.57</td>
</tr>
</tbody>
</table>

$J$-$V$ curves and the performance parameters corresponding to the best $J_{sc}$, $V_{oc}$, FF, and PCE after different days are shown in Fig.5 and Table 1, respectively. Our best $J_{sc}$ is 19.2 mA/cm², the best $V_{oc}$ is 1.0 V, the best FF is 0.65, and the best PCE is 10.2%. It can be found that the best value for each parameter appears at the different stages during the evolution period of the perovskite solar cells. This is due to moisture and oxygen in air affecting the performance of the individual parameters in the opposite directions. FF needs a certain time to achieve the best value caused by the oxidization of HTM, while $J_{sc}$ continues to decline caused by the decomposition of perovskite when it interacts
with moisture.

4. Conclusions

In conclusion, we compared the evolution characteristics of perovskite solar cells in air and vacuum environments. Each performance parameters of air-stored samples shows a drastic changes compared with that of the vacuum-stored samples. Moisture and oxygen in air are found to influence the perovskite solar cells performances together. HTM material needs to be oxidized to improve the conductivity, which will reduce the $R_s$ and in favor of FF. Perovskite is very easy to decompose once contact with moisture in air, leading to the decrease of $J_{sc}$. Therefore, the present findings will be a reference in the storage and evolutions of perovskite solar cells, and we believe the performance can be further improved with precise control of moisture and oxygen, which will be our next research topic.

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