Gas chromatography–mass spectrometry analyses of encapsulated stable perovskite solar cells

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Introduction

Although advances in materials and processing have led to remarkable advancements in the energy conversion efficiency of perovskite solar cells (PSCs), increasing from 3.8% to 25.2% in only 10 years, these solar cells cannot become commercially viable unless their underperforming durability is improved. The instability of perovskites must be addressed if PSCs are to compete with silicon technology, which currently offers a 25-year performance warranty. Previous approaches to this problem include the use of metal oxide barrier layers and butyl rubber sealants. Here, we report a low-cost polymer/glass stack encapsulation scheme that enables PSCs to pass the demanding International Electrotechnical Commission (IEC) 61215:2016 Damp Heat and Humidity Freeze tests. These tests help to determine whether solar cell modules can withstand the effects of outdoor operating conditions by exposing them to repeated temperature cycling (–40° to 85°C) as well as 85% relative humidity. Our airtight encapsulation scheme prevented moisture ingress. It was also effective in suppressing outgassing of decomposition products, which limits decomposition reactions of organic hybrid PSCs by allowing these reactions to come to equilibrium. The gas compositions were verified by gas chromatography–mass spectrometry (GC-MS).

Method

In the GC-MS technique, gas chromatography separates the components in a mixture, and the chemical identity of each component is determined with mass spectrometry (Figure 1). We could directly identify with high specificity the decomposition products of multi-cation perovskite precursors, of unencapsulated perovskite test structures, and of encapsulated full cells at elevated temperatures. The results allowed us to identify thermal degradation pathways by determining the outgassing products of mixed-cation perovskites during heating. We then used GC-MS to evaluate the effectiveness of different packaging techniques developed for PSCs. The packaging schemes were a polyisobutylene-based polymer (PIB) blanket encapsulation, a polyolefin-based polymer (PO) blanket encapsulation, and a PIB edge seal. These packaging layers were then capped by a glass cover. For the edge seal, the decomposition gases inside the cell were sampled with a syringe. The feasibilities of these packaging techniques were also demonstrated by IEC photovoltaic module standard Damp Heat and Humidity Freeze testing.

Results

Signature decomposition products such as CH_3I, CH_3Br, and NH_3 were identified and decomposition pathways were proposed for CH_3NH_3I (MAI), $HC(NH_2)_2I$ (FAI), CH_3NH_3Br (MABr), and mixed-cation and mixed-halide $(FAI)_{0.85}$ + $(MABr)_{0.15}$ perovskite precursors, including their secondary decomposition reactions at 350°, 140°, and 85°C. The GC-MS results confirmed that the Br-containing precursor was less prone to thermal decomposition than an I-containing precursor. Also, CsFAMA cells were found to outgas one-fifth as much decomposition product as their FAMA counterparts, which indicated that the Cs-containing cells had better thermal stability. Although the decomposition of FAI is reversible, the mixing of MA with FA precursors caused decomposition products to participate in the secondary reaction that was irreversible. This finding confirmed the disadvantage of mixing of MA with FA perovskite through the reduction in chemical stability. GC-MS found that by using polymer/glass blanket encapsulation, the thermal decomposition of PSC could be stopped, while there was still decomposition products detected in edge-sealed PSC (Figure 2). The blanket-encapsulated PSCs sustained no efficiency degradation after 1800 hours of Damp Heat testing or 75 cycles of Humidity Freeze testing (Figure 3). XRD results show that no change of PbI_2 peak amplitude before and after the Damp Heat testing (Figure 4). Sealing the PSC in a pressure tight environment effectively suppresses the decomposition reaction even when it is not fully reversible as in the case for MA or FA/MA mixed multi-cation perovskites.

Conclusion

GC-MS identified signature volatile products of the decomposition of organic hybrid perovskites under thermal stress, thereby informing decomposition pathways. The findings are important for developing potential cell-stabilizing strategies, given that cells in the field typically experience high operating temperatures. In addition, results of GC-MS confirm that the low-cost pressure-tight encapsulation we developed is effective in suppressing such outgassing and therefore decomposition reactions of PSCs. This encapsulation scheme is the simplest of all for perovskite cells to pass IEC photovoltaic module standard tests. Our approach can be applied to evaluating the effectiveness of other packaging approaches, as well as testing the effectiveness of coatings and material compositions aimed at limiting light and thermal degradation.

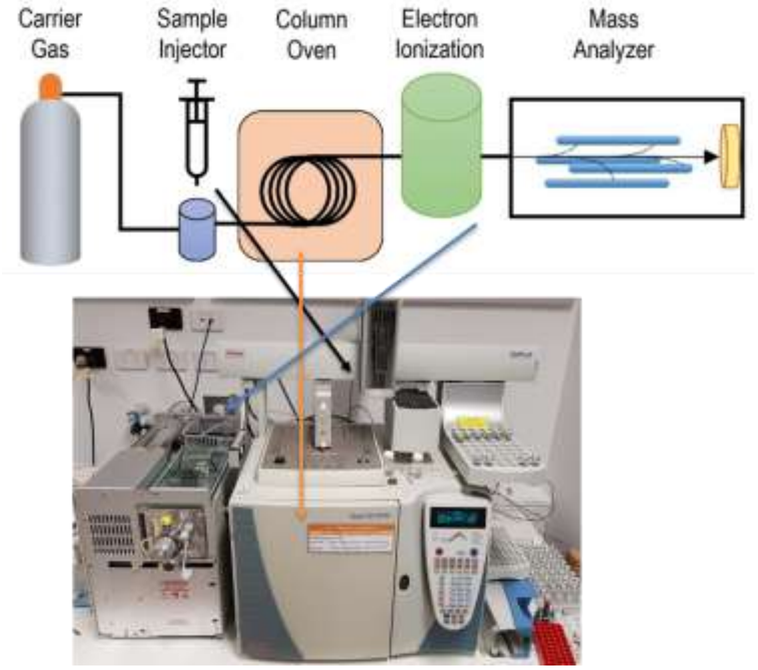

Figure 1. Work flow and photo of the GC-MS setup, Thermo Trace DSQ II Quadrupole GC-MS with Triplus HS autosampler (Thermo Scientific, Watham, MA)

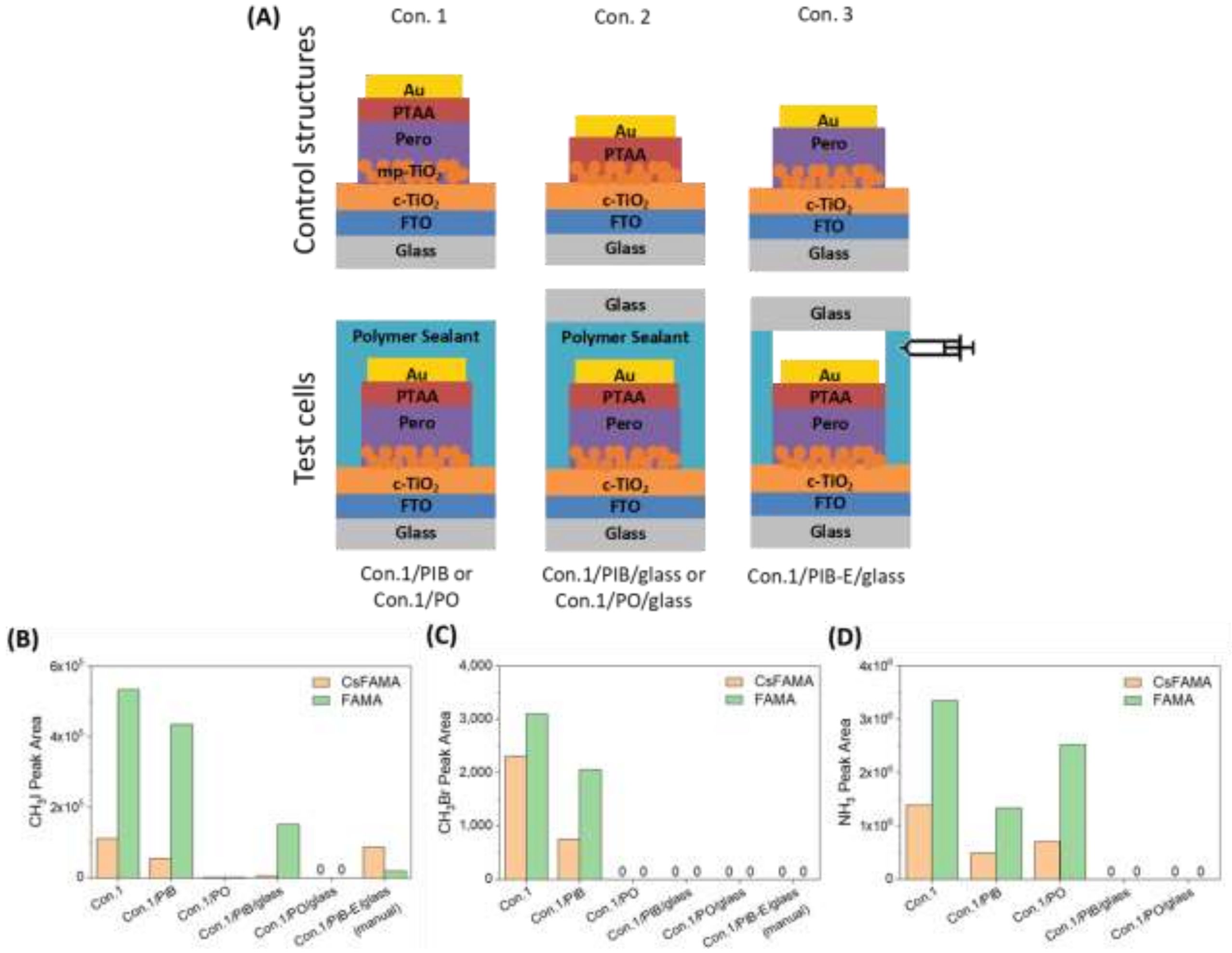

Figure 2. (A) Un-encapsulated test structures and encapsulated tests cells for GC-MS measurement (not to scale). A syringe is used for the "Con.1/PIB-E/glass" structure for manual gas sampling. "Pero" is either $Cs_{0.05}FA_{0.8}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$ or $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$.Signature decomposition products of un-encapsulated test structures and encapsulated tests cells. (B-C) GC-MS peak areas of the signature decomposition products of (B) CH_3I, (C) CH_3Br, and (D) NH_3 for 100-hour- 85°C-annealed PSC's with or without packaging

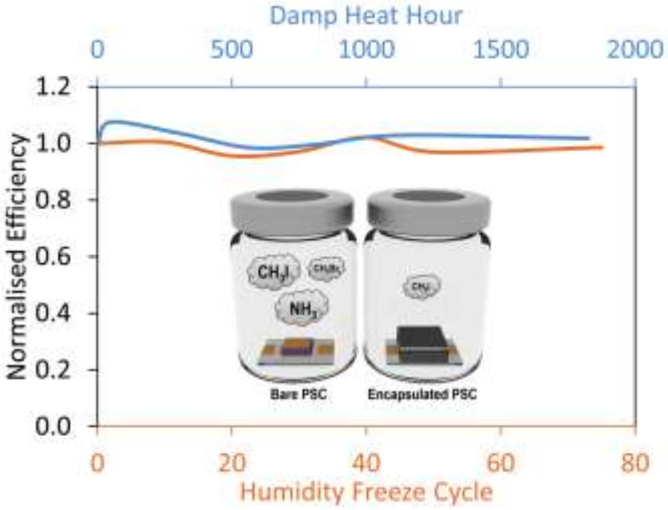

Figure 3. Stable perovskite solar cells exceeding the requirements of the IEC61215 Damp Heat and Humidity Freeze tests.

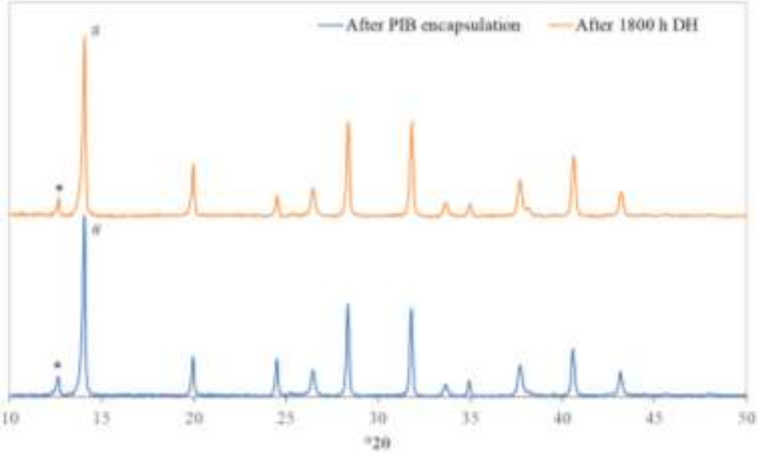

Figure 4. X-ray diffraction (XRD) analysis of PIB blanket encapsulated CsFAMA PSC before and after 1800 hours of Damp Heat test. * and # denote the PbI_2 and $Cs_{0.05}FA_{0.8}MA_{0.2}(I_{0.85}, Br_{0.15})_3$ perovskite characteristic peaks, respectively.