What does the HCN decomposition gas release tell us about the stability of formamidinium based perovskite?

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PSC is ...

- not a DSSC
- not a organic solar cell
- likely a light harvester as Si/CIGS/CdTe/GaAs based solar cell.

But a relevant difference...

Melting Points

Si 1414 °C

GaAs 1238 °C

CdTe 1092 °C

CIGS 990-1070 °C

There is no melting/boiling points in hybrid perovskite

Signature of “hybrid” dissimilar materials

Hybrid perovskite vs Organic solar cells

- Resemblance: Two materials blend, low T of decomposition
- Difference: 1) Random blend vs. ordered blend.
2) 2 vs. 1 components for photovoltaic effect

In this talk:

- Why T is probably* the most important cause to consider in achieving free degradation long term operational stability of devices
- Two methods to analyze *in vitro* and *in vivo* chemical and operational stability for PSCs.
- The challenging thermal decomposition of FA based perovskite

Causes of degradation

- Moisture
- Oxygen
- Light (UV)
- Temperature
- Bias
- Ion migration
- Defects...

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Received October 14, 1986

This paper is dedicated to Professor Douglas E. Ryan on the occasion of his 65th birthday

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Water and Oxygen

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Water and Oxygen

bond dissociation energy (enthalpy change) ΔH_f° ,
kJ/mol

➡ Pb—I	197
Pb—Br	247
Pb—Cl	301
Pb—Pb	339
Pb—S	346
➡ Pb—O	378

Handbook of chemistry. Dean & Lange. McGraw-Hill, 1999

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bond dissociation energy

- Pb—I
- Pb—Br
- Pb—Cl
- Pb—Pb
- Pb—S
- Pb—O

Handbook of chemistry. D

Water
&
Oxygen

Causes of degradation

- Moisture
- Oxygen
- **Light (UV)**
- **Temperature**
- Bias
- Ion migration
- Defects...

Photodegradation vs. Thermal degradation

PbI_2 band gap (2.34 eV, 530 nm)

450 + 550 nm
white

617 nm
red

470 nm
blue

Photodegradation vs. Thermal degradation

(1965) Dawood et al. The photodecomposition of lead iodide.

Photographic applications of PbI_2

Photodegradation in hybrid perovskite?

MAPbI₃ band gap (1.55 eV, 800 nm)

It implies:

→ All visible light and beyond (UV) will potentially damage PVK

J. Mater. Chem. A 2018, 6, 9604-9612.

ACS Appl. Mater. Interfaces 2019, 11, 12586-12593.

10.26434/chemrxiv.7295585

**Qualitatively, no
difference between
photodegradation and
thermal degradation tests**

**MAPbI₃
T < 82 °C**

J. Mater. Chem. A 2018, 6, 9604-9612.

10.26434/chemrxiv.7295585

The best approach at this moment:

- + Encapsulation
- + chemically inert SC
- + non-metal electrodes

Does it work?

Perovskite solar cells with operational output for 4000 h. TEMPERATURE is prevailing cause

- 1) Probably, it is the **longest MPP** test on perovskite solar cell ever reported (4000 h).
- 2) **No engineering composition**. They used exclusively MA cation on A position for the perovskite.
- 3) They **encapsulated** the devices.
- 4) **No UV filtering. No apparent damage by Bias (ion migration)**
- 5) Avoiding organic HTM.
- 6) Avoiding metal back electrode
- 7) High influence of **temperature** during the MPP stability test.

Fig.S6 Long-term stability test of the semitransparent device with NiOx HTL under 1 SUN. The device was kept at MPPT condition at various heat stresses in temperature controlled oven.

M. B. Islam, M. Yanagida, Y. Shirai, Y. Nabetani, K. Miyano, Sol. Energy Mater. Sol. Cells **2019**, 195, 323-329.

A paradigm shift in the search for more stable cells:

we should not ask “how long?”

but “what temperature threshold?”.

Stability assessment of PSCs

To determine the specific T threshold destroying irreversibly the device during MPPT.

For each configuration set

- 1) perovskite composition
- 2) selective contacts
- 3) metal electrode
- 4) encapsulation strategy

The promise of this method:

If a specific configuration allows T threshold higher than $> 85^{\circ}\text{C}$, probably it is enough for long standing commercial perovskite devices.

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

Lei Shi^{1,*}, Martin P. Bucknall^{2,3}, Trevor L. Young¹, Meng Zhang^{1,4}, Long Hu⁵, Jueming Bing^{1,6,7}, Da Seul ...

+ See all authors and affiliations

Science 21 May 2020:
eaba2412
DOI: 10.1126/science.aba2412

IEC61215:2016

- Damp Heat
- Humidity Freeze

Methods to Analyze Stability of Perovskite-Type Absorbers and Solar Cells (StabPero) · 13:00h UTC (15:00h CEST) June 2nd - 3rd, 2020

nanoGe
Online Meetup Conferences

nature
energy

CONSENSUS STATEMENT

<https://doi.org/10.1038/s41560-019-0529-5>

OPEN

Consensus statement for stability assessment and reporting for perovskite photovoltaics based on ISOS procedures

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ISOS-T-3	None	−40 to +85 °C	< 55% ^{b)}	Env. chamber	Solar simulator	OC
Light cycling (ISOS-LC)						
ISOS-LC-1	Solar simulator/ Dark Cycle	Ambient (23 ± 4 °C)	Ambient	Light only	Solar simulator	MPP or OC
ISOS-LC-2	period: 2, 8, or 24 h Duty cycle:	65, 85 °C	Ambient	Light & temperature	Solar simulator	MPP or OC
ISOS-LC-3	1:1 or 1:2	65, 85 °C	< 50%	Light, temperature & RH	Solar simulator	MPP
Solar-thermal cycling (ISOS-LT)						
ISOS-LT-1	Solar simulator	Linear or step ramping between room temp. and 65 °C	Monitored, uncontrolled	Weathering chamber	Solar simulator	MPP or OC
ISOS-LT-2	Solar simulator	Linear ramping between 5 °C and 65 °C	Monitored, controlled at 50% beyond 40 °C	Env. chamber with sun simulator	Solar simulator	MPP or OC
ISOS-LT-3	Solar simulator	Linear ramping between −25 °C and 65 °C	Monitored, controlled at 50% beyond 40 °C	Env. chamber with sun simulator and freezing	Solar simulator	MPP or OC
<p>Each test group is divided into three levels of sophistication that reflect the complexity of required equipment and the harshness of the applied stress. Reported ISOS protocols are taken from ref. ¹¹. Proposed additional ISOS protocols are printed in bold. ^aV_{OC}, V_{MPP}, and J_{MPP} are determined from light J-V curves measured under standard solar cell testing conditions on a fresh device. E_g and q are the band gap of the active layer and elementary charge, respectively. ^bRelative humidity is controlled at temperatures above 40 °C and is not controlled for the remainder of the cycle. Env., environmental; OC, open-circuit condition; MPP, maximum power point; RT, room temperature; RH, relative humidity.</p>						
ISOS-LT-4	Solar Simulator	Linear ramping between -25 °C and 120 °C	-	-	Solar Simulator	MPP

Highly stable semi-transparent MAPbI₃ perovskite solar cells with operational output for 4000 h

M. Bodiul Islam^{a,b,c}, M. Yanagida^a, Y. Shirai^{a,*}, Y. Nabetani^b, K. Miyano^a

TEMPERATURE
prevails over all of
causes of
degradation

Fig.S6 Long-term stability test of the semitransparent device with NiOx HTL under 1 SUN. The device was kept at MPPT condition at various heat stresses in temperature controlled oven.

In vitro stability of perovskites

Small Methods **2018**, 1800242.

Small Methods **2018**, 1800242.

Activation energy for the first mass loss step during induced thermal degradation of perovskites as descriptor of chemical stability of hybrid perovskites.

From Thermogravimetry (TG) Measurements

E_a (kJ mol⁻¹)

FAPbI ₃	115 ± 3
FAPbBr ₃	133 ± 1
MAPbI ₃	93 ± 8
MAPbBr ₃	98 ± 4
CsPbI ₃ ^a	650 ± 90

J. Mater. Chem. A **2019**, 7, 16912

In this talk:

- Why T is probably* the most important cause to consider in achieving free degradation long term operational stability of devices
- Two methods to analyze *in vitro* and *in vivo* chemical and operational stability for PSCs.
- FA based perovskite thermal decomposition

HCN release controversy

At the present time:

5 articles reporting HCN release from FA based perovskite.

Article	Year	Determination Method	Temperature	Comment
Song et al. Sustainable Energy & Fuels 2018 , 2, 2460	2018	MS	< 65	Overlooked as CNH*
Juarez-Perez et al. J. Mater. Chem. A 2019 , 7, 16912	2019	MS	50-100	
Ma et al. Chem. Mat. 2019 , 31, 8515	2019	FTIR	>360	Reverse trends
Akbulatov et al. Sol. Energy Mater. Sol. Cells. 2020, 213, 110559.	2020	MS	=300	Single shot T
Sei et al. Science, 2020, 10.1126/science.aba2412	2020	GC-MS	>350	

Formamidinium (FA) thermal degradation

J. Mater. Chem. A **2019**, 7, 16912-16919.

Formamidinium (FA) thermal degradation

J. Mater. Chem. A **2019**, 7, 16912-16919.

Advantages FA vs. MA

- 1) Higher thermal stability
- 2) No irreversible (non-selective) back reaction

J. Mater. Chem. A **2019**, 7, 16912-16919.

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Nanostructured Films and Particles
(Jesús Santamaría)

Instituto Universitario de Investigación
en Nanociencia de Aragón
Universidad Zaragoza

2015-2019 OIST (Japan)

Energy Materials and Surface Science
(Yabing Qi)

Japan Society for the Promotion of Science (JSPS)
KAKENHI Grant number: **17K14551**

Supporting Slides

Energy Environ. Sci. 2016, 9, 3406-3410.

J. Mater. Chem. A 2018, 6, 9604-9612.

ACS AMI 2019, 11, 12586-12593.

10.26434/chemrxiv.7295585

J. Mater. Chem. A 2019, 7, 16912-16919.

Acute exposure guideline level (AEGL) for the airborne concentration of HCN

AEGL-1 (8 h exposure) < 1 ppm

AEGL-3 (10 min exposure) < 27 ppm

Potentially 88 ppm for 1 m² active layer

According to our MS measurements: estimation of 0.002 ppm for 1 m² active layer (85 °C)

under these extreme vacuum and T conditions: ~ 4 hours to reach AEGL-1 in 1 m³ volume next to the panel.

- It adds problems choosing encapsulation type (indoor or outdoor panels)
- During manufacture process

フィリンをプロトホルファイリン置とよぶことがある。ホルファイリンは特有の吸収スペクトルを示し、紫外線照射により紅色の蛍光を発する。D環の17,18位が還元されたジヒドロホルファイリンをクロリン(chlorin)とよび、さらにC環も還元されたテトラヒドロホルファイリンをジヒドロクロリン(dihydrochlorin)という。

ホルファイリ錯体 [porphyrin complex] ホルフィン錯体(porphine complex)を母核とする誘導体の総称。金属ホルファイリン(metal porphyrin, metalloporphyrin)ともいう。ホルフィンそのものは天然には存在しない、その誘導体、すなわちホルファイリンは(2-)イオンとして錯体を

は皮膚に炎症、皮膚がんの発癌剤(αβ[2])として、現在までな作用を示しているのは、Cytosol ciplase L. (ハズ)の種子から単離された TPA (12-O-テトラデカノイルホルボル 13-アセート)である。

When it is boiled with aqueous potassium hydroxide, it generates ammonia and decomposes.

CH₂OH

TPA

十生成エンタルピーは 301 kJ/mol⁻¹。第一イオン化ポテンシャル 6.02 eV、電子親和力 ± 0.6 eV、電気陰性度(ポーリング) 1.1~1.2 程度。+IIIの酸化状態を生じやすく、性的酸化数をもつ安定化合物はほとんど知られていない。Ho³⁺ + 3e⁻ = Ho の標準電極電位は -2.319 V。Ho³⁺ のイ

塩(formamidine hydrochloride: 潮解性の結晶、融点 80 °C。水に易溶、エタノールに可溶。水酸化カリウム水溶液と煮沸するとアンモニアを発生して分解する。100 °C に加熱するとシアニ化水素と塩化アンモニウムに分解する。酢酸塩(formamidine acetate; CH₃NH₂-CH₂COOH)：オルト酢酸エチルと酢酸の混合物を 125~150 °C に加熱し、アンモニアを導通すると得られる。無色の結晶(無水エタノールから再結晶)、融点 162~164 °C。保存が容易で、ホルムアミジンが行う多くの反応に酢酸塩のままで使用できる。種々の複素環化合物の製造原料として重要。酢酸塩：針状晶(無水エタノールから再結晶)、融点 89 °C。ピタラ

Kagaku Jiten (Dictionary of Chemistry)

Ohki, M., Ohsawa, T., Tanaka, M. & Chihara, H. (Tokyo Kagaku Dojin, Tokyo, 1994) P.1381.

FACI
Decomposes into hydrogen cyanide and ammonium chloride when heated to 100 °C

ホルムアルデヒドをシアン化して調製する。プロロホルム-メタノール溶液から暗赤色結晶として晶出する。ピリジン、ジオキサン、フェニールに可溶、クロロホルムに微溶、アセトン、メタノールにほとんど不溶。ホルフィン環の水素が陽々の基で置換されたものをホルファイリンという。CAS[101-60-0]

ホルボルエステル [phorbol ester] トウダイグサ科(Euphorbiaceae)の植物から単離されたジアルベンの直鎖脂肪族のエステル類の総称。ジエステル型の多くのもの

(543, 300); 0.1 N NaOH 230, 292 nm (543, 338)。脂の白炭素病菌に有効である。ホルマイシンと異なり、in vivo でリン酸化を受けない。作用機序はプリンスレオシドホスホリラーゼの阻害である。消剤：マウス LD₅₀ (経口) 1000

ホルミルナフタレイン [formyl naphthalene] ニナフトアルデヒド
ホルミルヒドロペルオキシド [formyl hydroperoxide] = 過オキシ
ホルムアニリド [formanilide] = N-フェニルホルムアミド (N-phenylformamide)。C₇H₇NO、分子量 123.14。アニリンを HCONH- 酢酸水溶液と加熱して得る。無色結晶(リグロイン-キシレンから再結晶)、融点 46.6~47.5 °C (エーテル-石炭エーテルから再結晶)、沸点 271 °C, 216 °C (120 mmHg)。水、エタノール、ベンゼンに可溶。UV λ_{max} (nm(ε)) : 242~243(13,700; 96% EtOH), 239~240(11,200; 水), 240(12,600; シクロヘキサン)。CAS [102-70-8]

ホルムアミジン [formamidase] CH₃NH₂ 分子量 44.06。H₂N-CH₂-NH₂。ホルムイミド酢酸塩とアルコール性アンモニアとの反応で塩酸塩の形で得られる。遊離塩基は、水に易溶で吸湿性があり、また加水分解しやすいので結晶の形で知られていない。[誘導体] 塩酸

ホルムアルデヒドはアルカリを作用させるとカニッツァロ(Cannizzaro)反応*を起し、酢酸とメタノールを生成する。また、塩基触媒で数分子が結合して糖の混合物(ホルモース)が得られる。アンモニアと反応するとヘキサメチレンテトラミン(ヘキサミン、ウロトロピン)が得られる。工業的に重要な化合物でフェノール、尿素、メラミン、キシレン、トルエンなどと反応し重合体(熱硬化性樹脂)が得られる。[誘導体] セミカルバゾン：融点 129~131 °C の結晶。フェニルヒドラジン：融点 145 °C の結晶。2,4-ジニトロフェニルヒドラジン：融点 181 °C の黄色結晶。CAS[50-00-0]

ホルムアルデヒドオキシム [formaldehyde oxime] = ホルムアルドキシム(formaldoxime)。CH₂NO、分子量 45.04。CH₂=NOH。 ホルムアルデヒドとヒドロキシルアミンとの結合によりつくられる。三量体構造(図)をとる。沸点 84 °C。アルカリ性で、マンガン、銅、および鉄族元素と敏感に反応するので、検出試薬として使用される。五酸化リンと反応すると、シアニ化水素を発生するので取り扱いに注意が必要。CAS[75-17-2]

ホルムアルデヒドジエチルアセタール [formaldehyde diethyl acetal] = ジエトキシメタン(diethoxymethane)、ジエチルホルマール(diethylformal), エチラール(ethylal)。C₅H₁₂O₂、分子量 104.15。CH₃(OC₂H₅)₂。ホルムアルデヒド水溶液と塩化水素を含むエタノールに、塩化カル

Z. Song, C. Wang, A. B. Phillips, C. R. Grice, D. Zhao, Y. Yu, C. Chen, C. Li, X. Yin, R. J. Ellingson, M.J. Heben, Y. Yan
Probing the origins of photodegradation in organic--inorganic metal halide perovskites with time-resolved mass spectrometry
 Sustainable Energy & Fuels **2018**, 2, 2460-2467.

FAPbI₃ shows significantly lower emission of organic species
 mainly in terms of **CNH** and CNH₂ (**aminocarbyne fragments**)

a)

b)

How to improve operational stability ?

1. PVK SCs have to be **encapsulated** not only to avoid oxygen/moisture but avoid release of gas components.
2. Use hole/electron selective layers chemically inert enough against **HI, CH₃I, CH₃NH₂, NH₃, formamidine, HCN** and **I₂**.
3. MA⁺ deleterious gas products and irreversible (no selective) path of degradation
4. Better thermal behavior for **FA⁺** than **MA⁺** (experiments and theory) but release of **HCN** at PV T working conditions.
5. Chemical equilibrium solid/gas products. Efforts to obtain best crystalline material deposition = Efforts in vain?

PVK easy to prepare = PVK easy to destroy

We have to assume partial destruction during daylight
And promote recovering at night