

Example 3: Keeping Tin in Check (PhD, STEM)

Level and discipline: PhD, Materials Chemistry / Photovoltaics (STEM)

Word count of the sample: approximately 1,150 words

Context: A first-year confirmation-of-candidature proposal for a funded PhD studentship at a UK university, assessed by a three-person supervisory panel before the candidate was confirmed onto the doctoral register.

Keeping Tin in Check: Suppressing Sn(II) Oxidation in Lead-Free Perovskite Solar Cells Through Combined Additive and Barrier Engineering

Abstract

Tin-based perovskite solar cells offer a lead-free route to low-cost thin-film photovoltaics, yet they degrade within hours of air exposure because tin(II) oxidises to tin(IV). Lead-based perovskites already reach certified single-junction efficiencies above 26%, as tracked by the NREL Best Research-Cell Efficiency Chart, while their tin counterparts stall near 15% and lose most of that output within days. This project attacks the oxidation problem at two points at once. It tests a combination of reducing additives in the precursor solution and a low-temperature atomic-layer-deposition (ALD) barrier, asking if the two together can hold tin in the +2 state across 1,000 hours of operation. The work pairs standard device fabrication with operando synchrotron X-ray absorption spectroscopy, which tracks the tin oxidation state as a live film

ages rather than after the fact. The target is a device that retains 80% of its initial efficiency after 1,000 hours under continuous illumination. Success would strengthen the case for lead-free perovskite photovoltaics at manufacturing scale.

Annotation: The gap is pinned to a single chemical failure mode, Sn(II) oxidation, and the abstract commits to a falsifiable number, 80% retention at 1,000 hours, so the panel can judge success against a fixed bar. A proposal that promises merely to "improve stability" gives reviewers nothing to hold it to.

Introduction and background

Perovskite solar cells moved from laboratory curiosity to a credible thin-film technology across a single decade, and their efficiency now rivals established silicon. One obstacle blocks their path to market at scale, which is the lead content of the best-performing compositions. Regulators and manufacturers both treat soluble lead as a liability, so a lead-free alternative with comparable performance would open doors that the lead chemistry keeps shut.

Tin is the obvious substitute, because it sits directly below lead in the periodic table and forms perovskites with suitable optical properties. The chemistry comes with a penalty. Tin prefers the +4 oxidation state in air, and once Sn(II) converts to Sn(IV), the film fills with defects that kill device performance. Current tin devices often lose the bulk of their efficiency within a week. This project treats that oxidation step as the central problem a PhD can realistically solve, and it builds the entire plan around slowing or stopping it.

Annotation: The introduction narrows a broad field down to one tractable chemical reaction, which is how a doctoral scope gets defined. The panel wants evidence that

the student can see the difference between a field-sized problem and a thesis-sized one, and this framing supplies it.

Literature review

Three research threads set up the project: tin perovskite composition, oxidation-suppression chemistry, and device encapsulation.

Work on composition has shown that additives such as tin(II) fluoride reduce background defects and that mixed two-dimensional and three-dimensional structures resist moisture better than plain films. These gains improve the starting efficiency, though they slow the oxidation only modestly.

The second thread covers reducing agents added to the precursor. Several groups have demonstrated that a reducing environment keeps tin in the +2 state for longer, and the reported chemistries range across metallic tin powder, hydrazine vapour, and organic antioxidants. Most of these studies report results across short ageing windows of a few hundred hours and seldom confirm the oxidation state directly during ageing.

The third thread, barrier layers, has focused on blocking oxygen and water after the film is complete. Atomic layer deposition produces dense, thin oxide coatings at low temperature, and it has extended the life of lead perovskites. Its use on tin devices remains thin, because the deposition conditions can themselves oxidise an unprotected tin film.

The gap emerges at the junction of the three. Additives and barriers each help on their own, no published study combines a reducing additive with an ALD barrier tuned for tin, and almost none tracks the Sn(II)-to-Sn(IV) conversion as it happens. This project occupies that junction.

Annotation: The three threads converge on one gap, the untested combination plus the missing operando measurement, which keeps the review from reading as a catalogue of prior results. The observation that most ageing windows are short does real work, because it sets up the project's longer 1,000-hour protocol as a genuine contribution.

Research aims and objectives

The central hypothesis is direct: a reducing additive in the precursor, paired with a low-temperature ALD barrier, will suppress Sn(II) oxidation enough for a device to retain 80% of its initial efficiency across 1,000 hours of continuous operation.

Four objectives structure the work:

1. Screen three reducing additives for their effect on starting efficiency and initial oxidation state.
2. Develop a low-temperature ALD barrier that coats a tin film without oxidising it during deposition.
3. Track the tin oxidation state operando across the full ageing window for the best additive-plus-barrier combination.
4. Correlate the measured oxidation kinetics with device efficiency loss to produce a predictive degradation model.

Each objective maps onto one work package, and objective three supplies the measurement that tests the hypothesis directly.

Annotation: The objectives translate a single hypothesis into four lab tasks, each becoming a work package with its own output. Panels look for this one-to-one mapping, because it proves the plan can test the claim it makes rather than merely explore around it.

Methodology

The experimental programme runs across four work packages inside a nitrogen glovebox for all air-sensitive steps.

Devices are fabricated as standard n-i-p stacks, with the tin perovskite deposited by spin-coating from a precursor dosed with one of three reducing additives. Film quality is characterised by X-ray diffraction, photoluminescence, and scanning electron microscopy, and device performance by current-voltage sweeps under a calibrated solar simulator. The ALD barrier is deposited at under 80°C, and its growth conditions are tuned so the oxidant does not reach the perovskite before the first monolayers seal the surface.

The central measurement is operando X-ray absorption near-edge spectroscopy (XANES) at a synchrotron beamline, which reads the tin oxidation state live while a sealed device ages under illumination. A cheaper and more common route would be post-mortem X-ray photoelectron spectroscopy on films pulled at intervals, and that route was set aside deliberately. Post-mortem sampling destroys each film, cannot follow one device through its whole life, and risks oxidising

the sample during transfer, which is the exact process under study. Operando XANES follows a

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single device continuously and removes that artefact. Ageing follows the ISOS-L-1 stability protocol so the results compare directly with the published literature.

Annotation: The operando-versus-post-mortem comparison is the heart of the method case, since the obvious cheaper technique would corrupt the very measurement the project depends on. Beam time is scarce and must be justified, so naming the artefact that only the live measurement avoids is what wins the allocation.

Timeline

The project runs across a 42-month full-time PhD.

Phase	Months	Work
WP1	1-12	Additive screening, baseline devices, first-year confirmation
WP2	10-22	Low-temperature ALD barrier development
WP3	20-34	Operando XANES ageing campaigns (two beam-time allocations)
WP4	30-40	Degradation modelling and correlation

Write-up 38-42 Thesis drafting and submission

Annotation: The beam-time campaigns are placed only after the barrier is working, which protects the scarcest resource against wasted allocations. A go/no-go point at the first-year confirmation lets the panel redirect the work early, and showing that point signals that the student plans for failure as well as success.

Expected outcomes and significance

The thesis will deliver three results. The first is a ranked comparison of three reducing additives against both starting efficiency and oxidation resistance. The second is a validated low-temperature ALD process that coats tin perovskite without oxidising it, reported with the full deposition window. The third is an operando dataset of the Sn(II)-to-Sn(IV) conversion across 1,000 hours, which becomes a predictive degradation model other groups can apply to their own compositions.

The significance reaches past the single device. A working combination of additive and barrier would give the lead-free perovskite field a route past its main stability barrier, and the operando method would give the wider community a tool for watching oxidation as it runs. Two journal articles and a conference presentation are realistic secondary outputs.

Annotation: Each outcome is a concrete artefact: a ranking, a validated process, a reusable dataset and model. The operando dataset offers value past the thesis, which strengthens the case that the project contributes a method and not only a result.

References (illustrative, ACS style)

1. National Renewable Energy Laboratory. Best Research-Cell Efficiency Chart.
<https://www.nrel.gov/pv/cell-efficiency.html> (accessed 2026).
2. Noel, N. K.; et al. Lead-free organic-inorganic tin halide perovskites for photovoltaic applications. *Energy Environ. Sci.* 2014, 7, 3061-3068.
3. Khan, M. T.; et al. Stability strategies for tin halide perovskite solar cells. *Adv. Energy Mater.* 2023, 13, 2300089.