

Immobilized redox mediators for Li-air batteries

Novel functionalised cathode materials to mitigate battery degradation



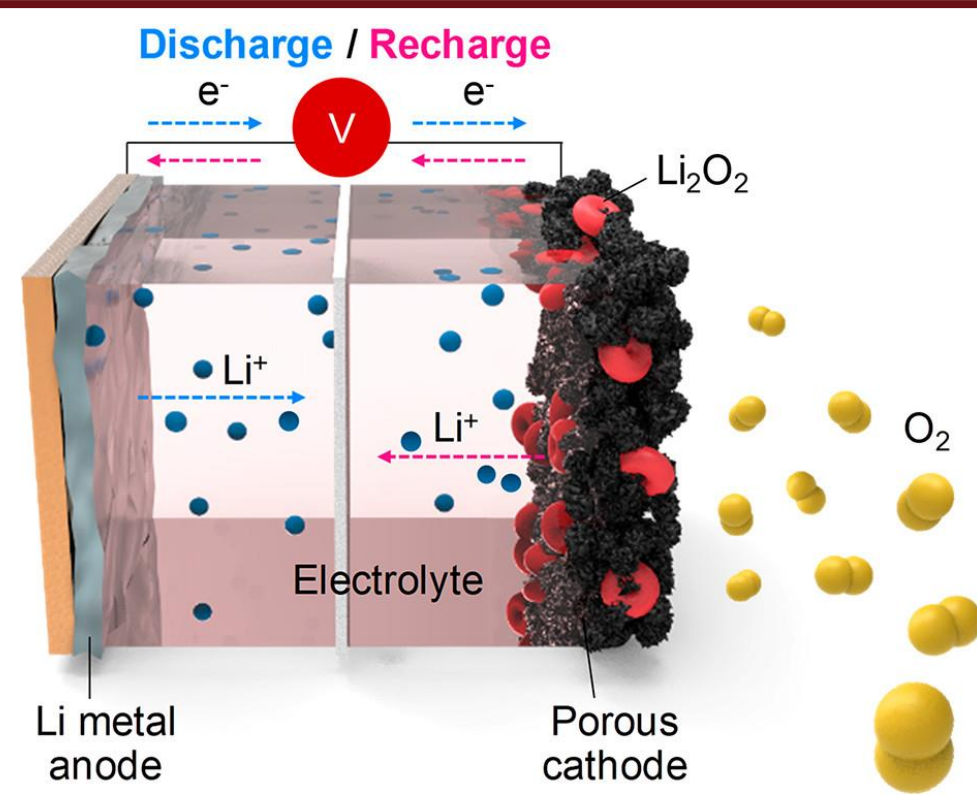
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Abstract

- Li-air batteries have been touted for their **high theoretical specific energy** and high operational voltage (2.96 V)
- Practical challenges of high overpotential and low capacity were addressed with addition of **redox mediators**, but this introduced further **degradation** associated with redox shuttling
- Herein, we demonstrate that redox shuttling can be mitigated by **immobilising** redox mediators to the cathode surface

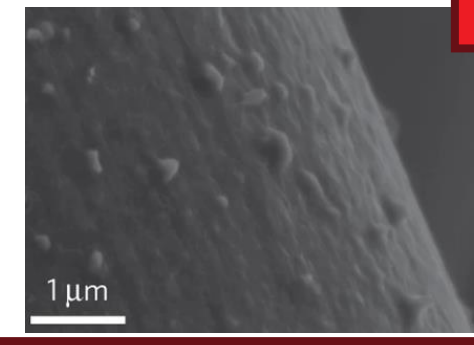
Li-air – background¹

- Li metal anode, porous air cathode, aprotic electrolyte with lithium salt
- During discharge, O₂ is reduced at the cathode to LiO₂ then Li₂O₂
- Li₂O₂ is insoluble and precipitates either as a thin film or large toroids



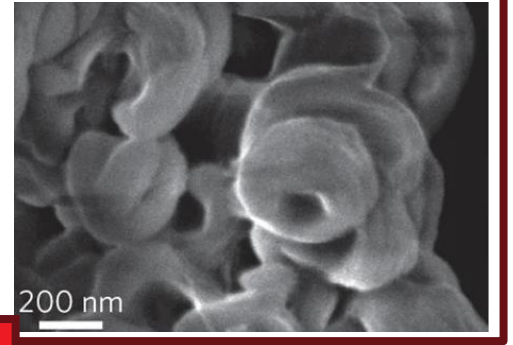
Li-air – problem

- If LiO₂ is poorly soluble, then reduction to Li₂O₂ occurs **near the surface**, forming a passivation layer
- The capacity is limited by the thickness of the passivation layer



Solution: redox mediators

- Redox mediators (RMs) act as an electron carrier to move reduction reactions further **into the solution**
- Thus, large **toroidal** particles grow, improving capacity²



Solution: immobilised RMs

Does immobilising RMs to the cathode

- Confer the advantages of solution-mediated discharge?
- Mitigate the ill-effects of redox shuttling?

RMs – new problems

- Redox shuttling:** RMs can migrate to the anode and cause
 - Self-discharge
 - SEI degradation
 - RM decomposition

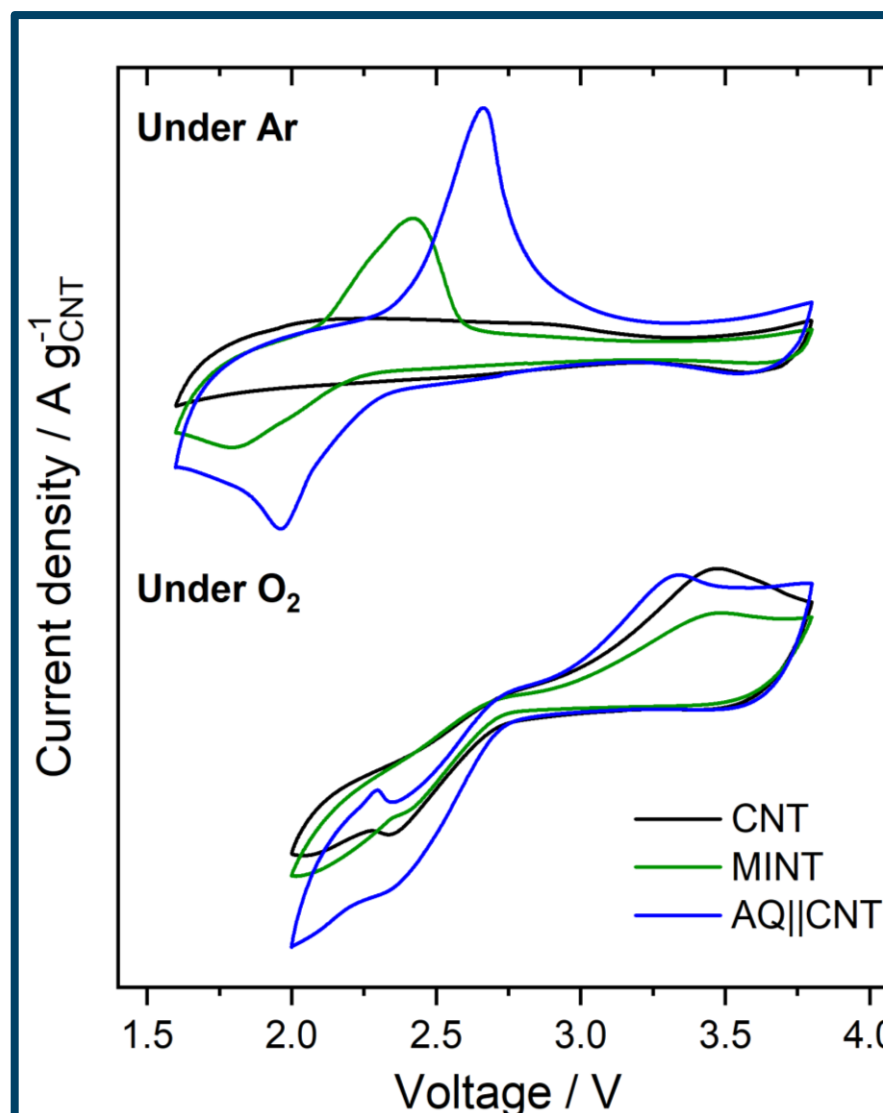
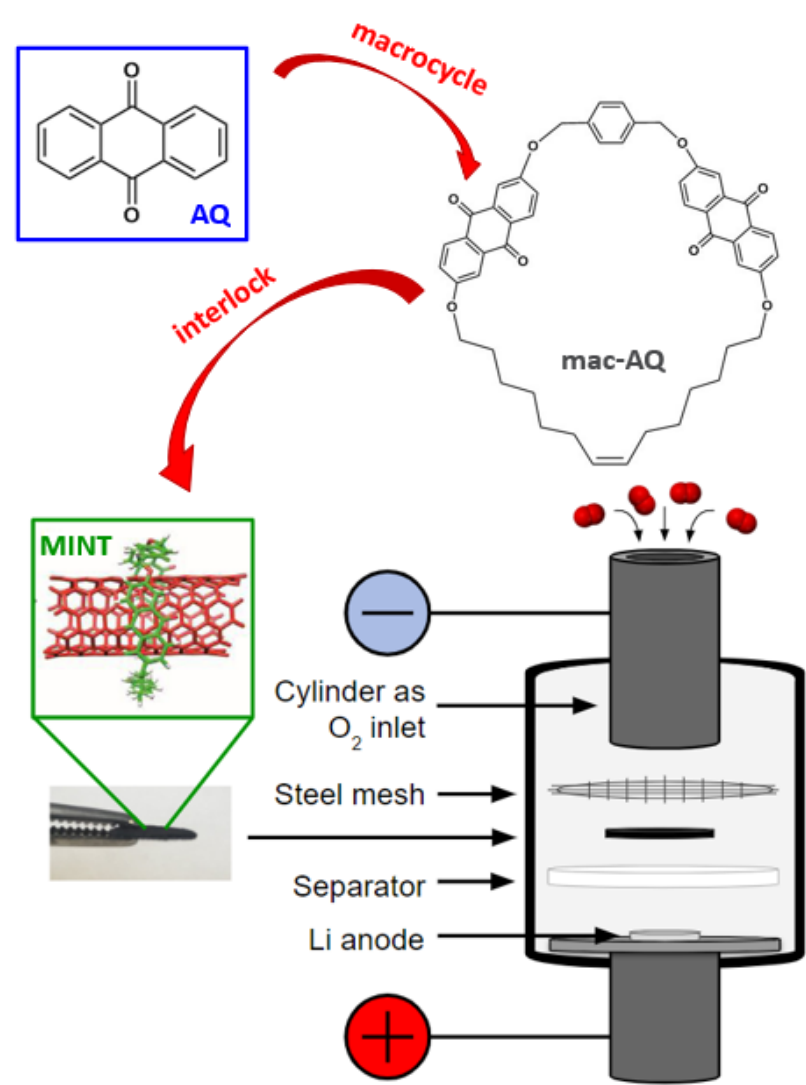
Methods – cell setup

CNT: Unfunctionalised carbon nanotubes as cathode

MINT: Anthraquinone (AQ) Mechanically-Interlocked on NanoTubes as cathode³

AQ||CNT: Free AQ in electrolyte, with CNT as cathode. Same amount of AQ in solution as amount of AQ units on MINT

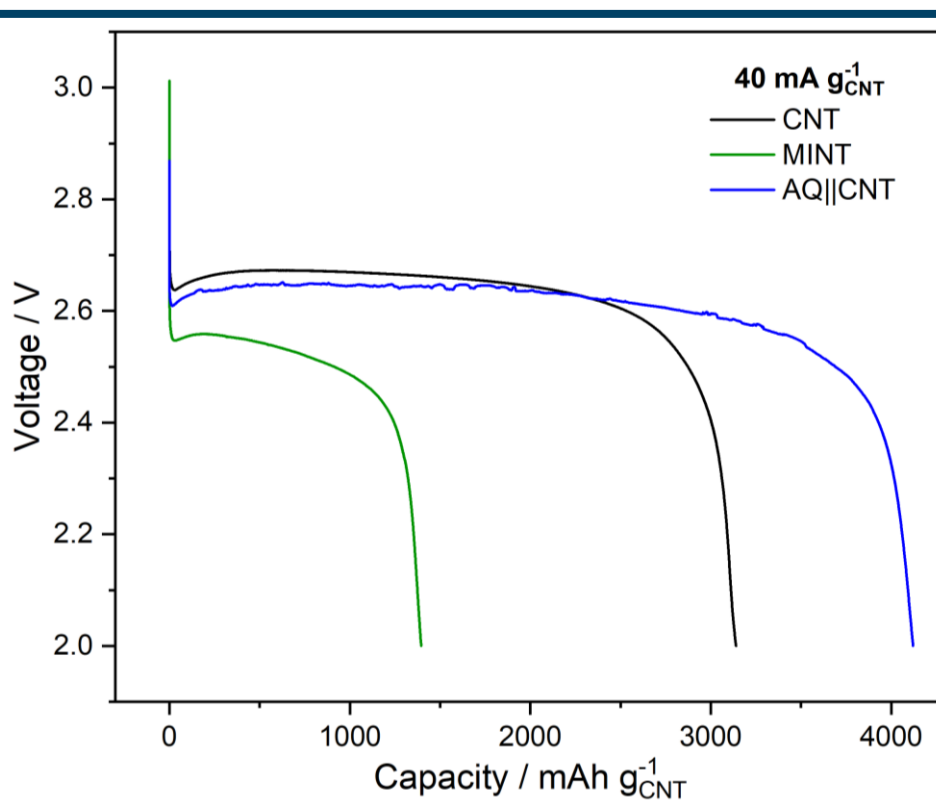
Electrolyte: 300 μL of 0.25 M LiTFSI in TEGDME



Electrochemical characterisation

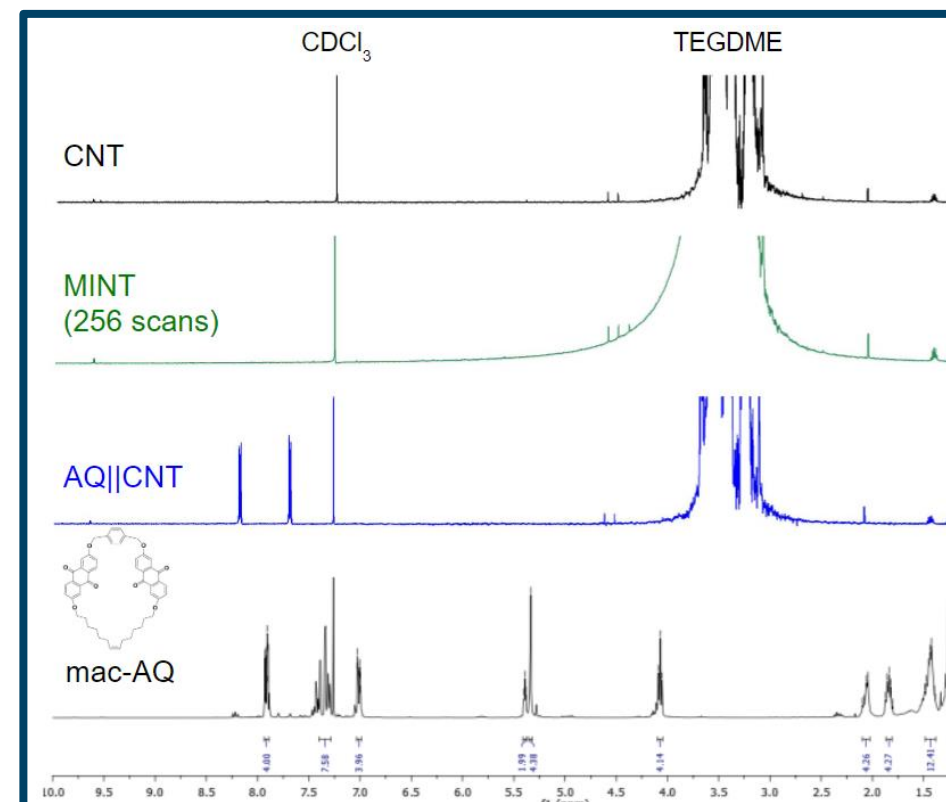
Two-electrode CV setup, WE: cathode, CE+RE: Li anode $v = 1 \text{ mV s}^{-1}$. Cycle 2 of CV under Ar or O₂

- Q/Q^{•-} couple evident for **MINT** & **AQ||CNT** under Ar
- Cycling stability:** **MINT** CV curves are similar after 40 cycles; **AQ||CNT** peak current decreases with cycling
- Potential of **MINT** is more negative than **AQ||CNT** due to electron-donating effect of ether oxygens
- AQ** shows enhanced O₂ reduction rate indicative of redox mediation, but **MINT** shows no enhancement
- Possibly due to the low potential of **MINT**, which can be altered by functional group modification



Discharge

Deep discharge to 2V at 40 mA g⁻¹ CNT
Large cell-to-cell variability precludes comparisons of capacity and overpotential



NMR of electrolyte

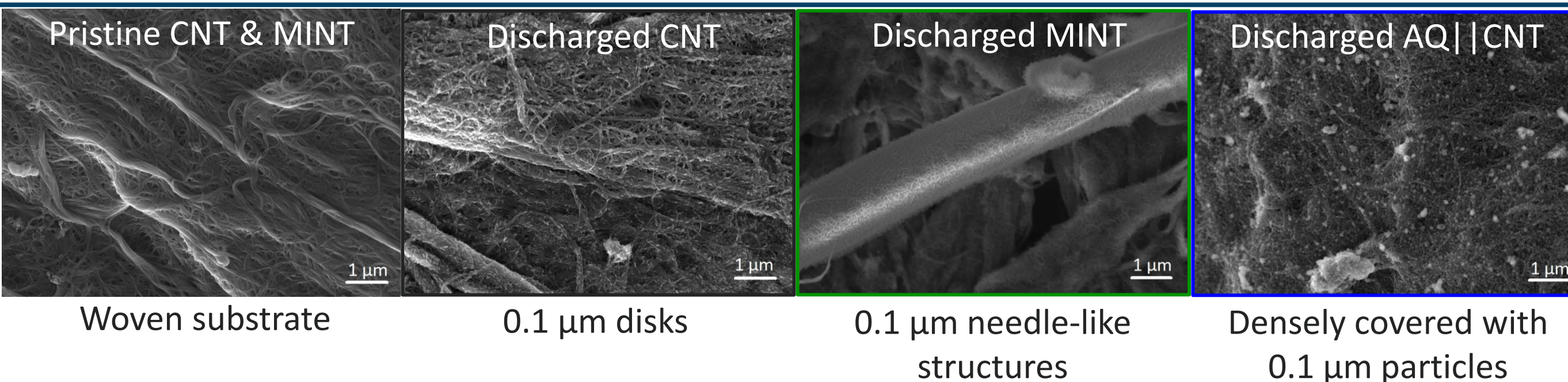
After discharge, separator soaked in CDCl₃ then NMR taken - ¹H NMR (500 MHz)
MINT: No evidence of mac-AQ in electrolyte. Immobilisation prevents RM from migrating to the anode

Conclusions

- Mechanically-interlocking to carbon nanotubes is a **robust immobilisation strategy**, conferring cycling stability and no detectable amount of detachment
- Redox active molecules retain their electrochemical properties even in MINT, and **functional groups** affect the redox potential
- Using AQ as an RM, MINT does not display the redox mediating effects of free AQ
- However, the discharge product morphology of MINT differs from CNT, indicating that the presence of mac-AQ molecules **affects the discharge mechanism**

SEM

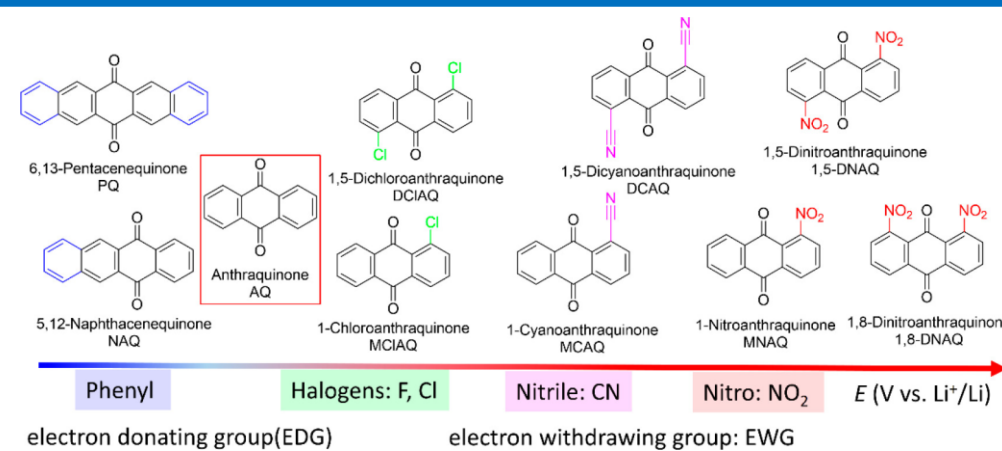
MINT alters morphology of discharge product
XRD data reveals crystalline Li₂O₂ for all three cells



Impact / Next steps

This proof of concept opens the doors for other RMs to be immobilised

- AQ derivatives with **electron-withdrawing groups** increase the redox potential with respect to the potential of O₂ reduction.⁴ mac-AQ with -NO₂ groups will be immobilized and tested
- Degradation caused by redox shuttling will be investigated with various **in-situ techniques** such as operando gas evolution analysis and **in-situ** NMR and EPR
- DFT calculations** have been initiated to investigate mechanisms of redox mediation



References

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Intern bio

I am a 3rd year chemistry student at the University of Cambridge. I am passionate about novel climate technologies such as energy storage solutions, carbon capture devices, and CO₂-to-fuels. Contributing to pioneering work in the DEGRADATION project has solidified my interest in materials chemistry and characterization techniques. Using spectroscopy, I hope to better understand mechanisms of catalysis, electron transfer, and degradation in novel materials for tackling climate related problems.

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