OPTIMISING CAPACITY RETENTION OF Li-O_2 BATTERIES

Using redox mediators and graphene-containing electrodes

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ABSTRACT

- Li-O_2 cells have **higher theoretical energy density** than current Li-ion batteries, potentially **low cost** and absence of finite transition metal usage.
- The critical issue to address is **poor capacity recovery**, as a result of **electrolyte and electrode degradation** caused by **high overpotentials.**
- 3 aspects were focused on to optimise capacity recovery: cycling **protocols**, **electrolyte**, **cathode**.

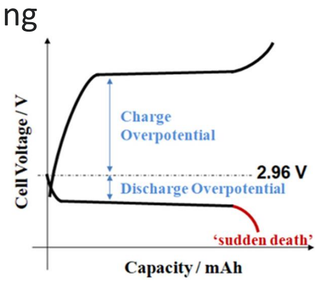


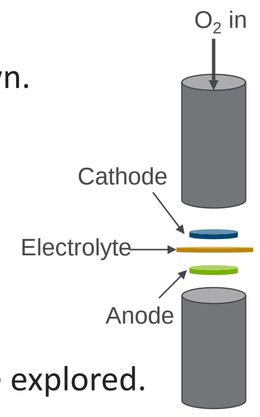
Figure 1: Capacity vs Cell voltage of a typical Li-O_2 cell.[1]

MOTIVATIONS

- A **CCCV** (constant current, constant voltage) charging protocol was developed to **reduce overpotential** and hence increase capacity recovery.
- **Redox mediators**, intermediates for electron transfer in solution, reduce overpotential and increase capacity retention by driving discharge product precipitation away from the electrode surface.
- Graphene's **high surface area** and **high electrical conductivity** make it a desirable additive to carbon electrodes.

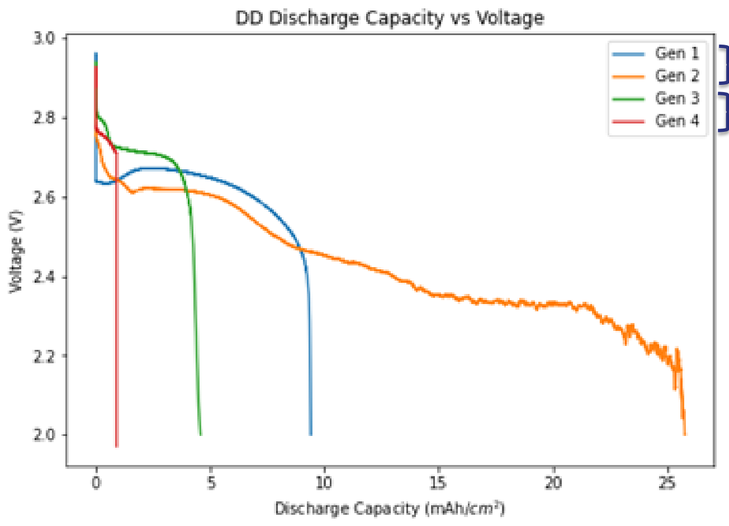
METHODS

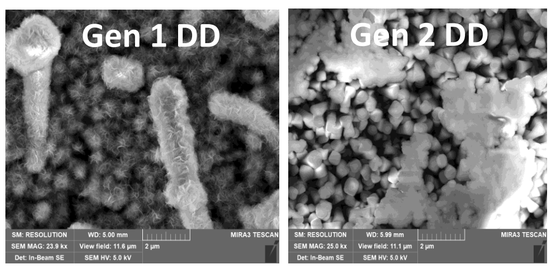
- 4 generations of Li-O_2 cells were assembled as shown.
- 3 cycling protocols were used to test cells:
  - A routine **deep discharge** limited at < 2 V
  - A **CCCV** charging protocol was developed to increase capacity retention
  - **CCCV x 10** cycles
- A range of **upper cut-off voltages** on the CCCV were explored.
- **SEM** and **XRD** were used to characterise discharge products.



Generation	Electrode	Electrolyte
1	Super P carbon/GDL	1M LiTFSI in DME
2	Super P carbon/GDL	1M LiTFSI + 0.1M LiI in DME
3	75% sP/25% graphene (90% nanoplatelets/10% PTFE)	1M LiTFSI + 0.1M LiI in DME
4	75% sP/25% graphene	1M LiTFSI + 0.1M LiI in DME

RESULTS - Discharge

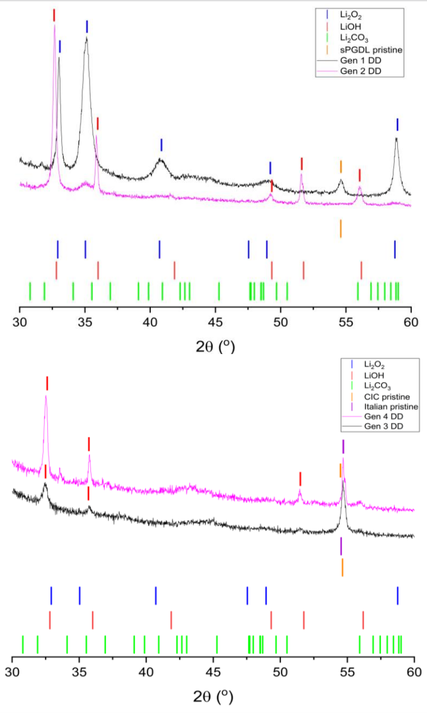




Typical LiOH flower-like crystals

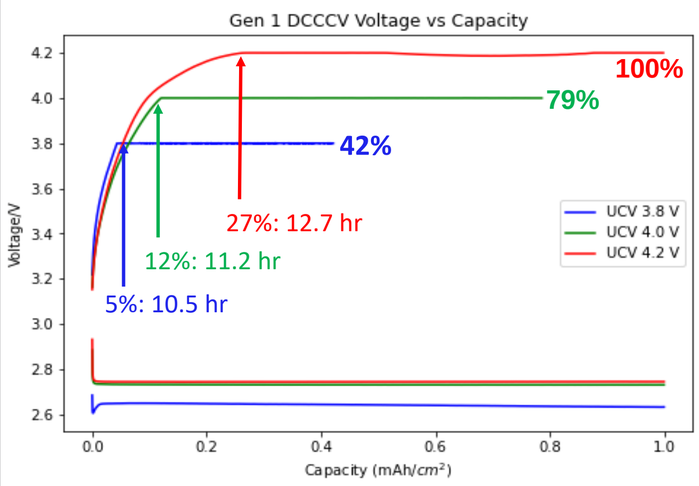
2 different crystal morphologies

Vertical columns of layered square crystals: nucleation promoted by I^-

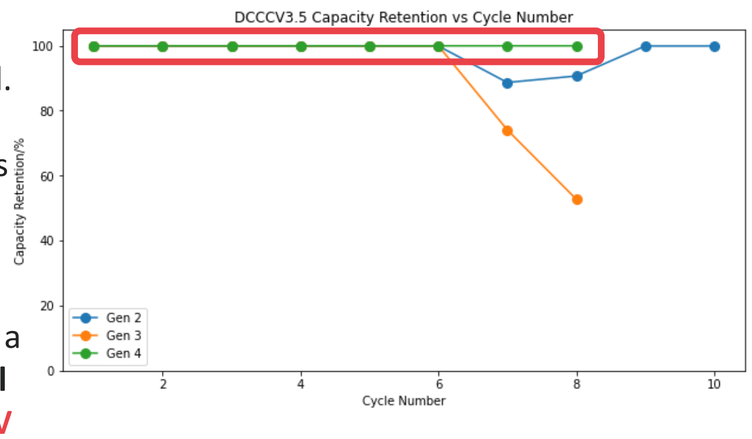


- **Electrolyte:** Addition of redox mediator, I^-, hugely increased discharge capacity - repeatability to be verified, given anomalous discharge profile.
  - **Gen 1:** XRD suggests Li_2O_2, SEM suggests LiOH: possible **mixture of Li_2O_2 and amorphous LiOH** (invisible to XRD).
  - **Gen 2:** XRD suggests LiOH, SEM difficult to conclude.
- **Cathode:** Addition of graphene decreased discharge capacity - repeatability to be verified as result contradicts expected increased discharge capacity due to graphene's higher SA.
  - **Gen 3 and 4:** XRD and SEM suggest LiOH.

RESULTS - Charge



- As UCV was increased, capacity recovery increased. The charging rate is faster before CV is reached, so it is favourable for maximum capacity to be recovered before CV. However, **I^- is oxidised to I_2** above 3.55 V, a reactive species causing **cell degradation**, so **UCV = 3.5 V** was found as optimal for fast charging whilst minimising overpotential and degradation.



- Over 10 cycles, **Gen 4** showed the greatest capacity retention per cycle, on results obtained so far.

CONCLUSIONS

- Capacity-limited CCCV protocols were optimised to maximise capacity recovery, charging rate, and minimise overpotentials.
- Redox mediators increased capacity recovery.
- The presence of visible discharge product in cells after charge, despite 100% capacity recovery, suggests **< 100% cell efficiency** or **degradation product** formation.

IMPACT / NEXT STEPS

- Graphene-containing electrodes will be optimised by varying parameters such as **graphene type** and **amount**, in order to maximise **surface area** and **pore size** to allow larger discharge product crystal growth.
- Graphene-containing cells will be run for **200+ cycles** to test the scalability of high capacity recovery and observe **cell degradation** over time.
- **Operando XRD**, **operando gas evolution analysis**, and **titration** will be carried out to characterise discharge products more **quantitatively**.
- The electrolyte will be optimised to further reduce overpotential by testing different redox mediators such as **quinones**, or **additives** such as water and ionic liquids.

REFERENCES

1. Adapted from Liu, T., Vivek, J., Zhao, E., Lei, J., Garcia-Araez, N. and Grey, C., 2020. Current Challenges and Routes Forward for Nonaqueous Lithium–Air Batteries. *Chemical Reviews*, 120(14), pp.6558-6625.
2. Temprano, I., Liu, T., Petrucco, E., Ellison, J., Kim, G., Jónsson, E. and Grey, C., 2020. Toward Reversible and Moisture-Tolerant Aprotic Lithium-Air Batteries. *Joule*, 4(11), pp.2501-2520.

INTERN BIO

I am a 2nd year chemistry student at The University of Oxford. My primary interests lie in the fields of inorganic and physical chemistry, particularly when applied to renewable energies and efficient energy storage solutions. Learning about the many obstacles to commercialisation of Li-air batteries for EVs has inspired me to want to pursue a career in chemical research applied towards helping achieve the UK's ambitious goal of net-zero greenhouse gas emissions by 2050.

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