Probing Parasitic Gas Evolution in Sodium Ion Batteries

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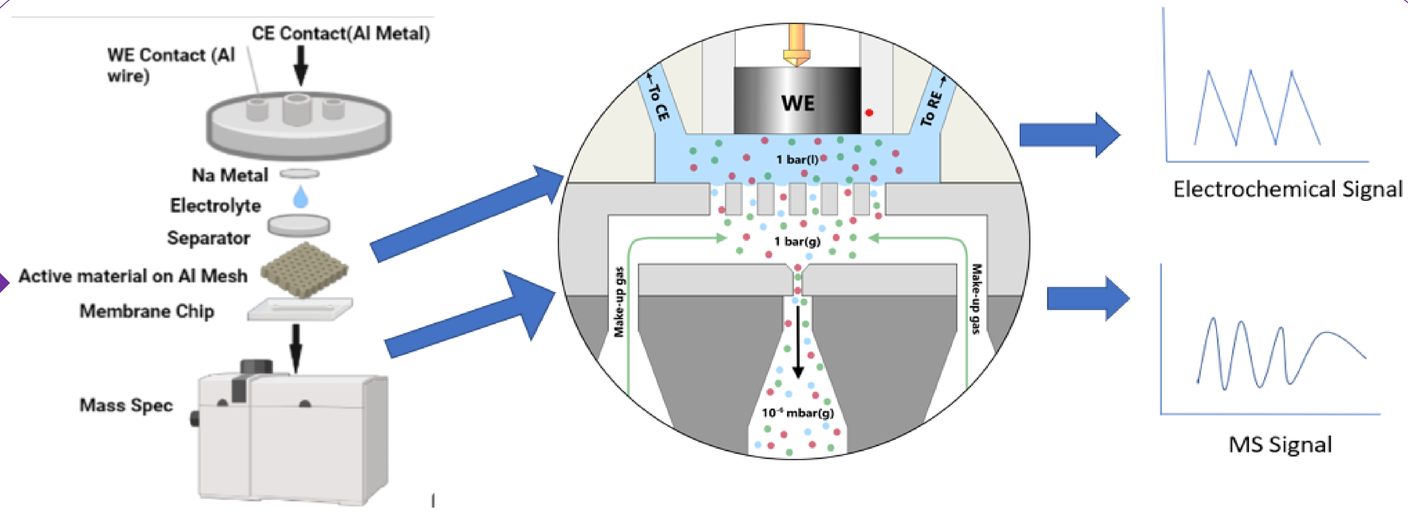
Motivation

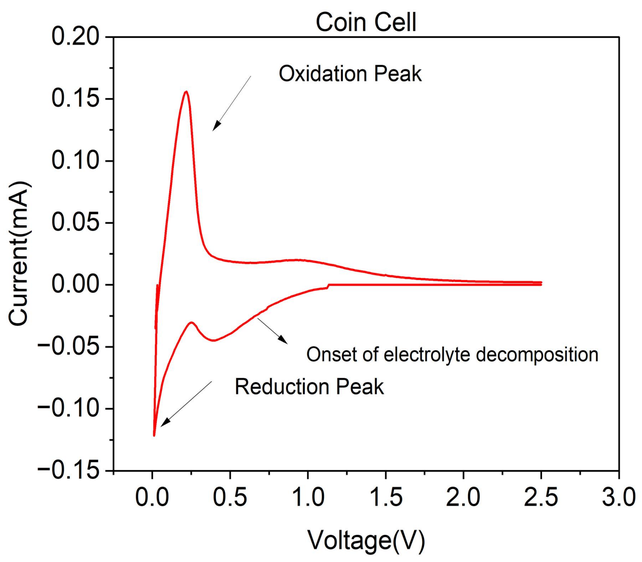
- Sodium ion batteries are considered a viable alternative to lithium ion batteries
- These batteries degrade by decomposition of the electrolyte and gas evolution hence, studying the gas evolution mechanism is important
- In-situ and In-operando mass spectroscopy techniques are a great way to study this degradation
- However, current techniques cannot detect very small quantities of volatile species and are therefore not very representative of battery degradation mechanism

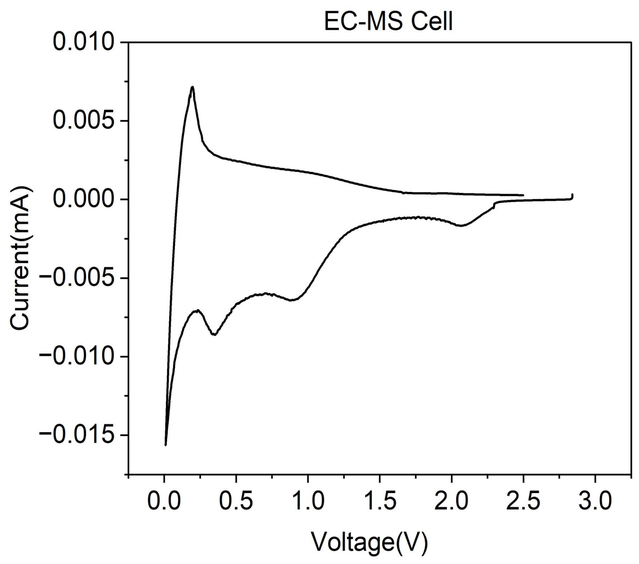
Solution- Electrochemistry Mass Spectroscopy (EC-MS) on a Chip!



- Developed and used for aqueous electrochemistry , recently adapted for non-aqueous electrochemistry and use in batteries.(1)(DB Thornton et al)
- Picomole sensitive technique, allowing for detection of very small amounts of volatile species previously undetected in batteries and above current state of the art.

Benchmarking EC-MS Cell compared to Coin Cell

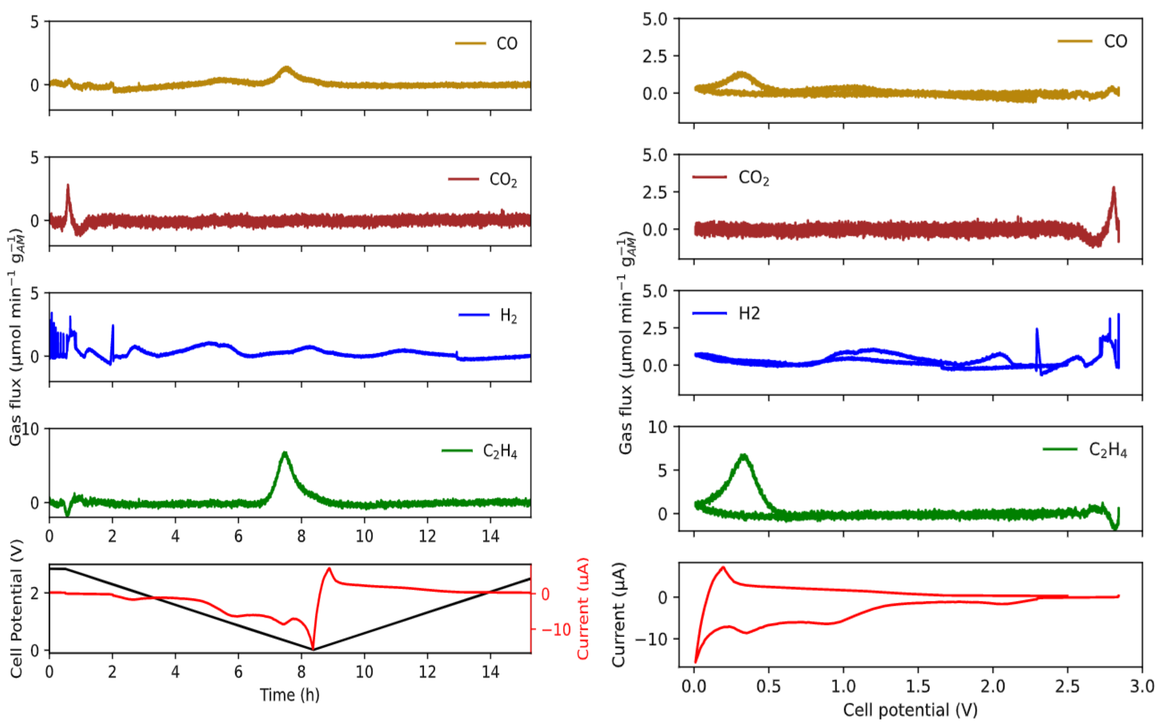




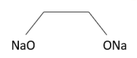
Electrolyte- $NaPF_6$ EC:DEC
Working Electrode- Hard Carbon
Counter Electrode- Na Metal

- Optimised the designed cell for EC-MS to ensure reproducibility compared to the coin cell benchmark for G1500 hard carbon against sodium metal.(2)
- Oxidation and reduction peaks (also considered sodium insertion and extraction peaks) observed for both cells at around 0V.(2)
- Onset of electrolyte reduction peak observed for both cells close to 1V

Gas Evolution In Sodium Ion Battery



CO Corresponding to decomposition of ethylene carbonate to form the SEI.

$C_3H_4O_3 + 2Na^+ + 2e^- \longrightarrow$  $+ CO$

CO_2 formed at open circuit potential while the cell is at rest. No CO_2 observed when cell begins to cycle possibly due to decomposition of CO?

$C_3H_4O_3 + H_2O \longrightarrow C_2H_5O_2^- + CO_2$

H_2 formation Due to decomposition of trace H_2O in contact with Na metal,

$H_2O + e^- \longrightarrow OH^- + ½\ H_2$

C_2H_4 formed at full discharge (0V) attributed to decomposition of ethylene carbonate

$C_3H_4O_3 + Na^+ + e^- \longrightarrow ½(CH_2COONa)_2 + C_2H_4$

$C_3H_4O_3 + 2Na^+ + 2e^- \longrightarrow C_2H_4 + Na_2CO_3$

Left- Potential, Current and Gas Flux against Time
Right- Current against Potential

- Maximum 10umol/min C_2H_4 (This work) detected vs 1umol/min max.(3)
- Maximum 1umol/min CO detected(This work) vs 0.2umol/min max.(4)

Electrolyte- $NaPF_6$ EC:DEC
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Counter Electrode- Na Metal

Conclusion

The EC-MS is an excellent technique to study gas evolution in battery systems, and has proven to be a few orders of magnitude more efficient in detecting volatile species previously undetected in other mass spectrometry systems.

Acknowledgement

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