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Gas Evolution Out of Mixed-Acid Flow Batteries

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Motivation:

Mixed-acid electrolyte (H_2SO_4 and HCl) provides improvements on standard electrolyte (H_2SO_4 only) for vanadium flow batteries

- Increases vanadium solubility
- Increases stable temperature window

However mixed-acid system Can produce significant amounts of Cl_2 gas

Fielded systems have had issues with Cl_2 generation

- Deformation of storage tanks
- Loss of primary containment

Cl_2 evolution needs to be properly characterized to prevent future incidents

Cl_2 gas is a safety hazard to people and environment

- Max 60min dose is 3ppm

Cl_2 plus H_2 is an explosive mix

- Very easy to initiate the reaction: Spark, Interaction with catalyst, UV light, High Temperatures, etc

	Standard (H_2SO_4)	Mixed Acid (H_2SO_4 and HCl)
Vanadium Solubility	1.6M	2.5M
Energy Density	25 Wh/L	35 Wh/L
Temperature Range	10 to 40C	-5 to 50C

Cl_2 + H_2 + Ignition source => $2Cl^-$ + H_2 => 2HCl

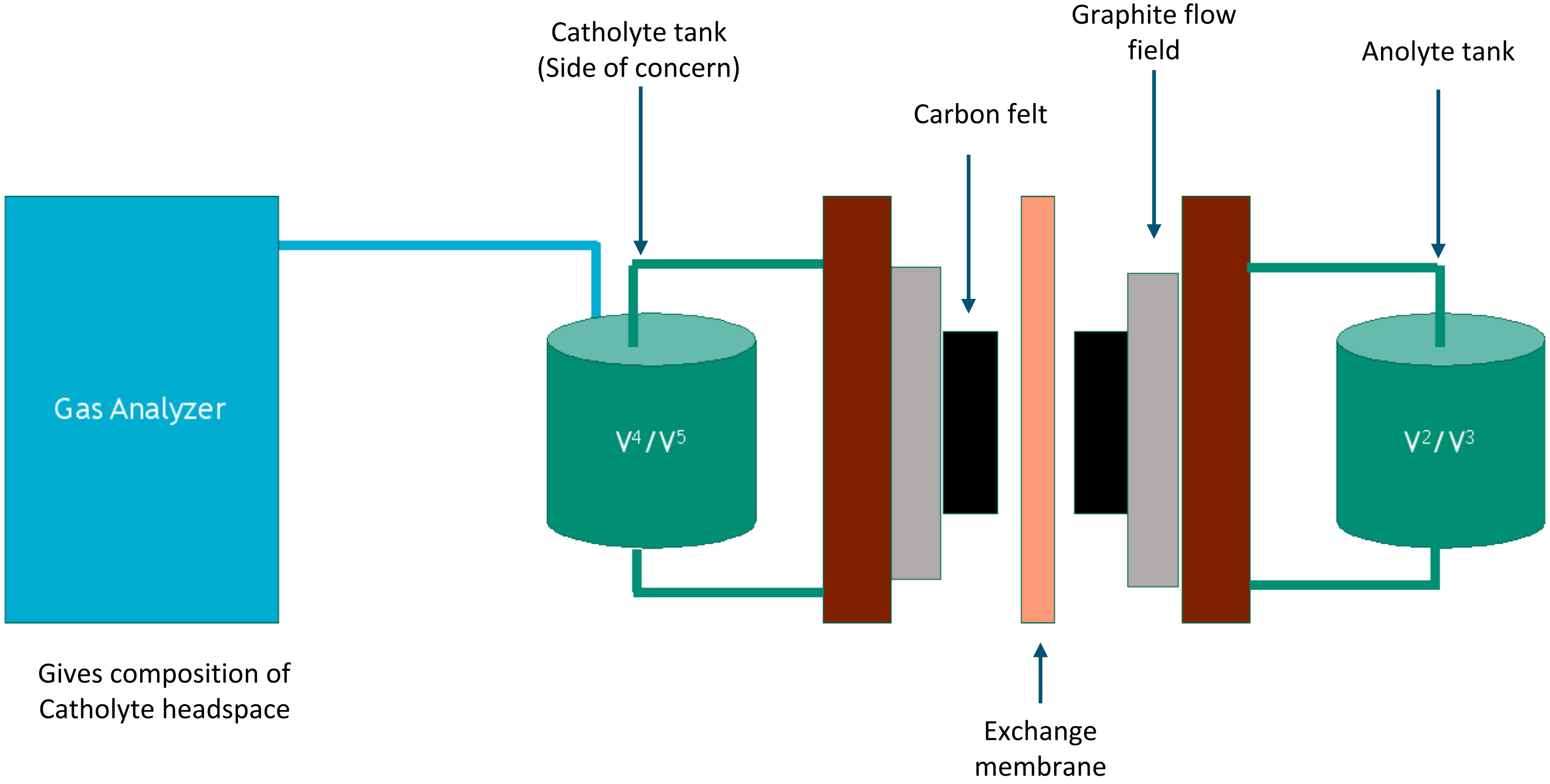
Releases 184kJ per mole

Small scale test setup

Can precisely control:

- Flow rate
- Current density
- Cell potential
- Temperature
- Impurities

Directly determine what conditions cause gas evolution



Full Cell reaction:

$$VO^{2+} + V^{3+} + H_2O \Leftrightarrow VO_2^{+} + 2H^{+} + V^{2+}$$

E = 1.26V

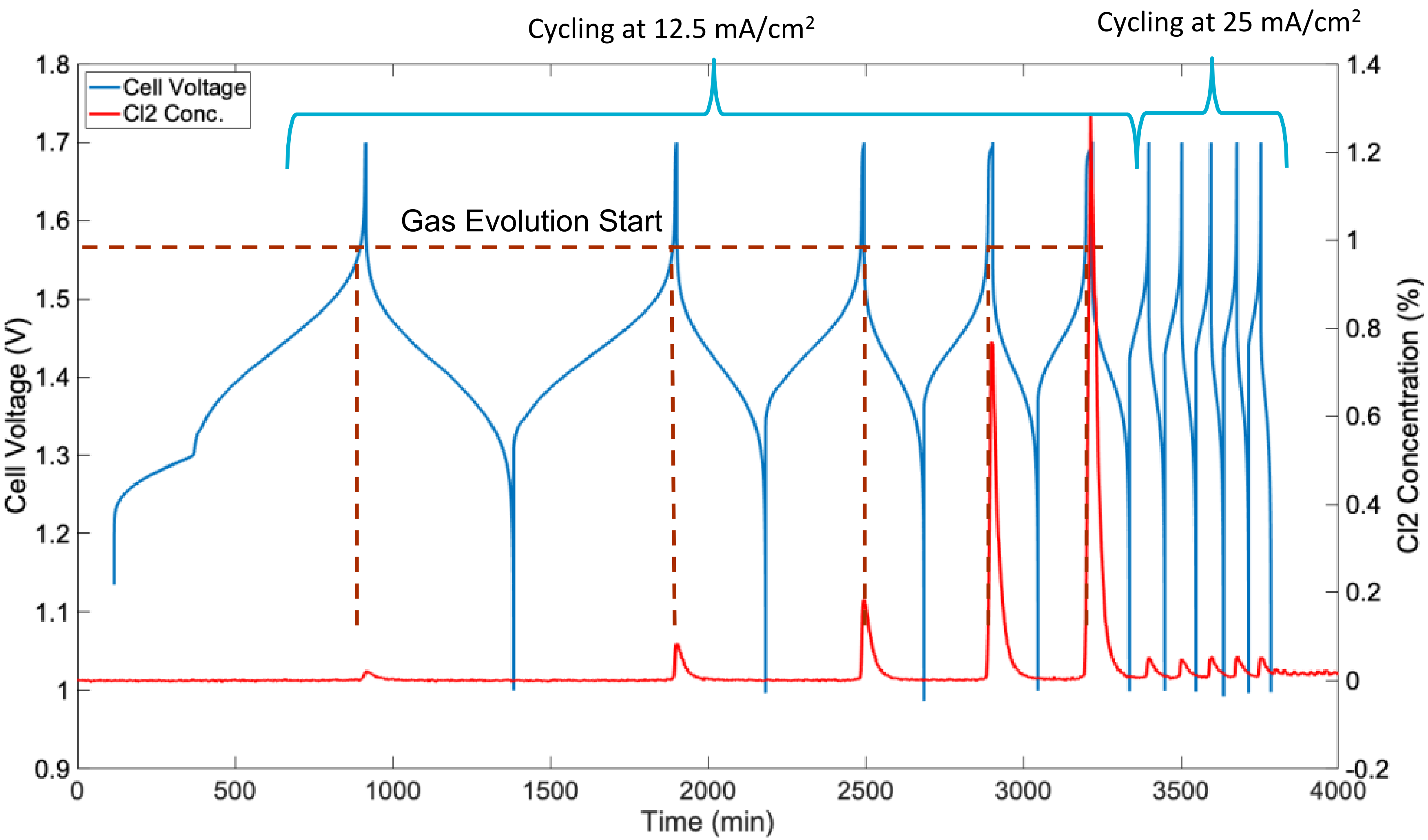
Gas evolution can occur near high charge

Tracking Cl_2 as percent of gases sampled by UGA

Cl_2 evolved at high SOC during charging

Also appears to increase as cycling becomes less efficient

Removed rapidly during discharge (likely reabsorbed into electrolyte)



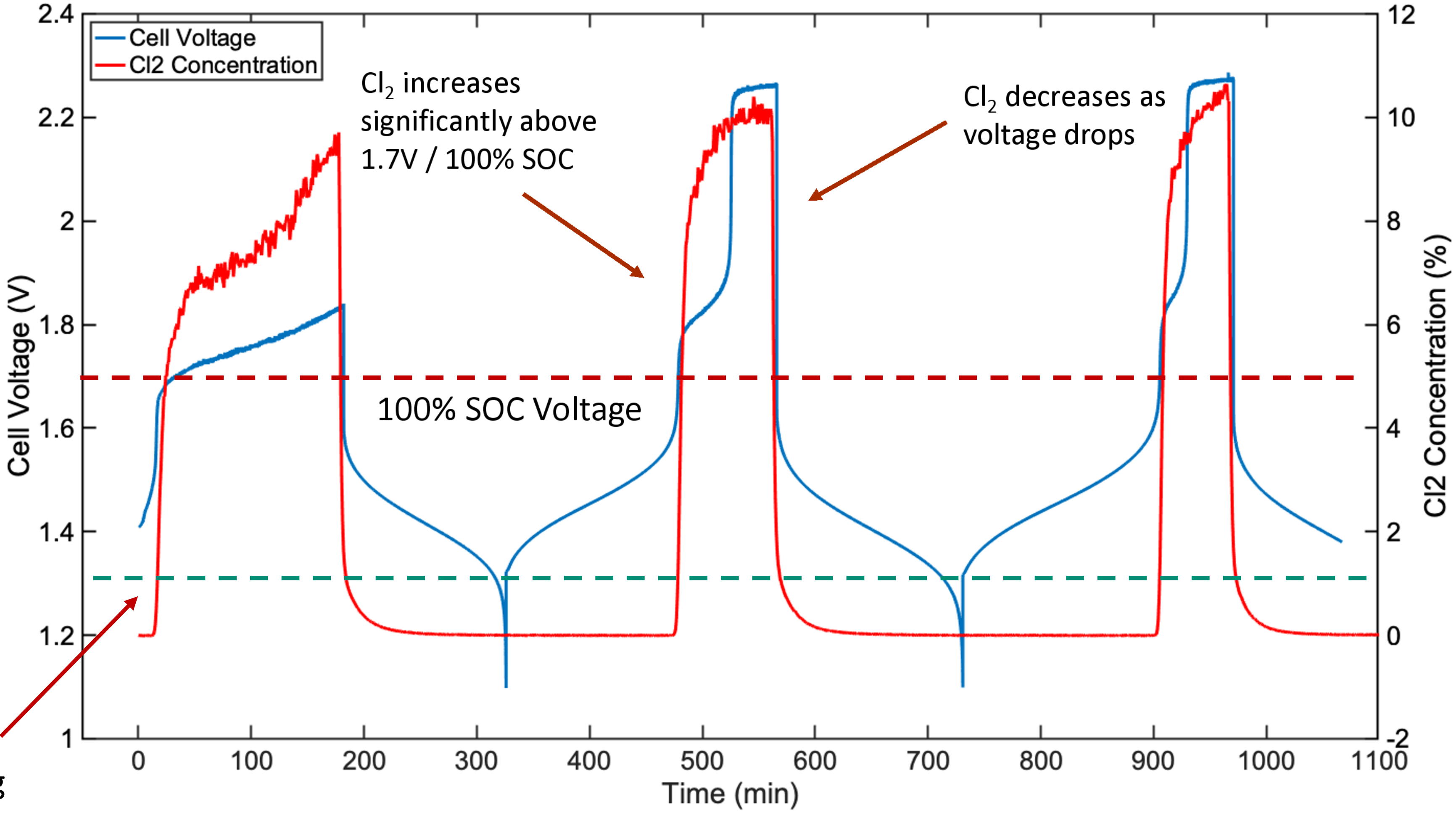
Any amount of over charging produces significantly more Cl_2 than normal operation

Cell voltage allowed to go above 1.7V (100% SOC)

V^{4+} should all be converted to V^{5+} at this condition

Side reactions are the only way to produce desired current

Favors Cl_2 generation



Max Cl_2 concentration during normal charging

Conclusions:

Cl_2 appears to be generated when cell voltage is above ~1.55V

Higher voltages can increase the amount of gas evolved

Studies are on the small scale and if rates of Cl_2 generation scale with electrolyte volume and electrode area, Cl_2 accumulation in large systems could easily achieve unsafe levels

- Overcharge experiment scaled to 1MW/4MWh could produce 4,750L (16% of the headspace)
- 1.7V hold experiment scaled to 1MW/4MWh could produce 3,500L (12% of the headspace)

Initial results suggest the following are viable mitigation strategies:

Operational

- Limit SOC range
- Prevent high cathode potentials

Environmental

- Increase headspace of system
- Consume Cl_2 as it is generated

Publications and Presentations:

Upcoming Publication: “Characterizing Cl_2 Gas Evolution out Mixed-Acid Flow Batteries” R. Wittman, H. Pratt, R. Poirier, T. Anderson, Y. Preger, *to be Submitted Spring 2022*

Invited Talk “Gas Evolution from Mixed Acid Flow batteries” Co-authors: Harry Pratt, Travis Anderson, and Yuliya Preger. ECS Spring 2021 Virtual Meeting

“Overview of Aqueous Battery Safety and Reliability Concerns” at the 2021 Energy Storage Systems Safety and Reliability Forum virtual meeting on April 20, 2021. https://www.sandia.gov/ess-ssl/wp-content/uploads/2021/ESSRF/4_Wittman_Reed_S1.pdf

“Grid-Scale Energy Storage Systems: Ensuring Safety”, B.R. Chalamala, D. Rosewater, Y. Perger, *R. Wittman*, J. Lamb, A. Kashiwaura, IEEE Electrification Magazine, Dec 2021, *Accepted*

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