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Gas Evolution from Mixed-Acid Vanadium Redox Flow Battery

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Introduction of aqueous battery safety

Aqueous Batteries (ABs) have long been pitched as a *safer* alternative to Li systems

However *safe*r does not mean *safe*

ABs have associated risks that need to be considered during system design

- Gas Evolution
- Thermal Runaway
- Electrolyte Containment
- System Level Safety

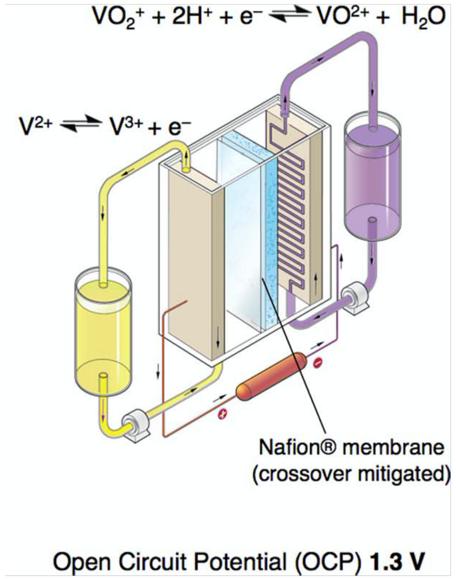
Perspective - On the Need for Reliability and Safety Studies of Grid-Scale Aqueous Batteries, RM Wittman *et al* 2020 *J. Electrochem. Soc.* **167** 090545

Flow battery safety

Thermal runaway is not considered a problem

1 MWh system can require 10,000 Gallons of electrolyte per side*

- Significant amounts of H_2 can be generated during cycling
- Other gases possible with different chemistries



Representative 2MW/8MWhr Vanadium Redox Flow battery system

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*Based on energy density of 25wh/L K. Lourenssen et al, J. Energy Storage, 25 (2019)

Mixed acid vs sulfuric based vanadium redox flow battery

Standard vanadium redox flow battery uses high molarity sulfuric acid as electrolyte

- Vanadium species are not equally stable
- Has a relatively low energy density
- Limited temperature range

H_2SO_4 and HCl electrolyte mix can improve performance

- Correct mixture (2.5 SO_4 5M HCl) can achieve equal solubility of each vanadium species
- Increases electrolyte energy density overall
- Increases stable temperature window

	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

Mixed acid vs sulfuric based vanadium redox flow battery

Standard vanadium redox flow batteries generate H_2 on the anolyte side during charging

- H_2 is considered a significant combustion risk above 4% concentration in a system

Mixed electrolyte systems can produce Cl_2 gas on the catholyte side as well as H_2 on the anolyte side

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

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

Releases 184kJ per mole

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Fielded mixed acid 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

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Releases 184kJ per mole

Potential mechanisms for Cl_2 gas generation

Electrochemically as a side reaction during charging in the catholyte side of the FB system

- $2Cl^- \Rightarrow Cl_2 + 2e^-$ (1.35V at STP, 1M HCl)

Chemically as a self discharge reaction in the catholyte

- Potentially: $VO_2^+ + 2H^+ + Cl^- \Rightarrow VO^{2+} + H_2O + 1/2Cl_2$

Partial pressure based evaporation (Henry's Law)

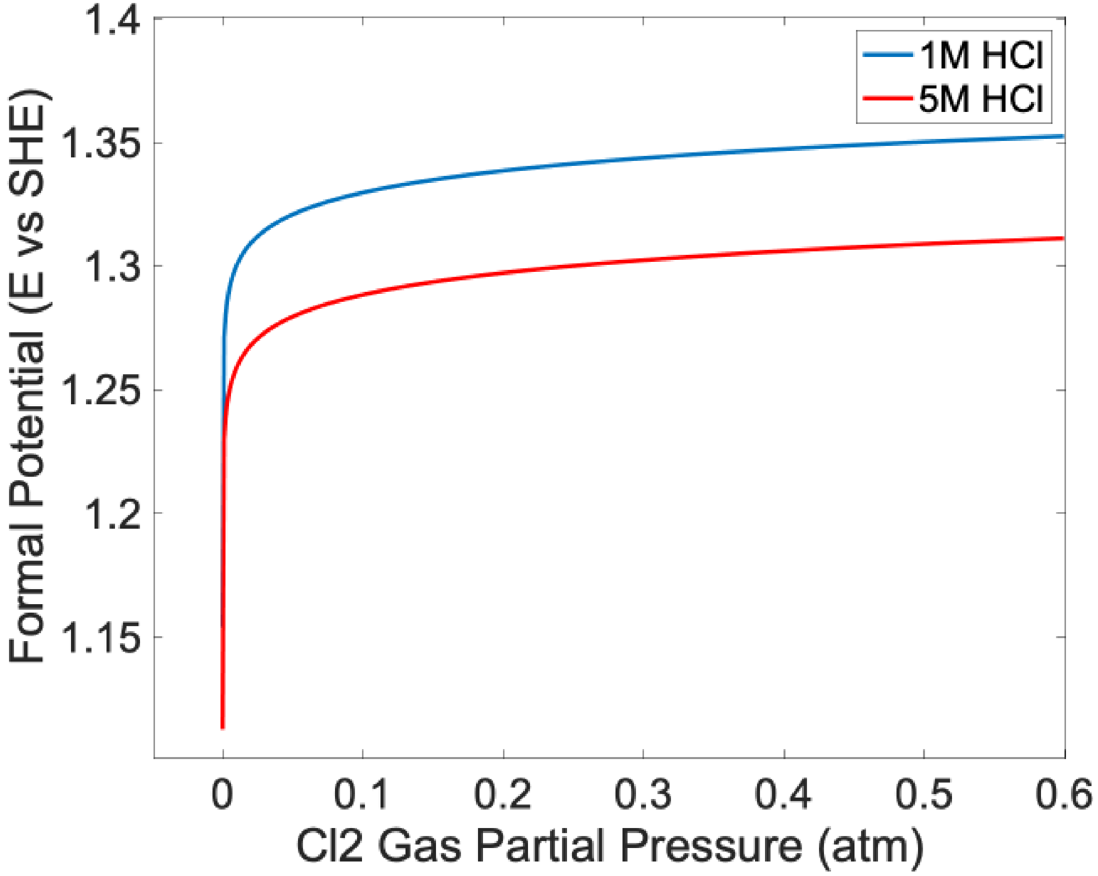
- $C_{Cl2(g)} = kP_{cl2(g)}$

Gas evolution can be influenced by a number of variables

- Temperature
- Solution chemistry
- Head space composition
- Catalyst/ impurities
- Cycling conditions
- Electrode material
- System impurities

Need to be able to control these variables to accurately study the gas evolution reaction

Influence of HCl Concentration and Cl_2 gas partial pressure on $2Cl^-/Cl_2$ formal potential

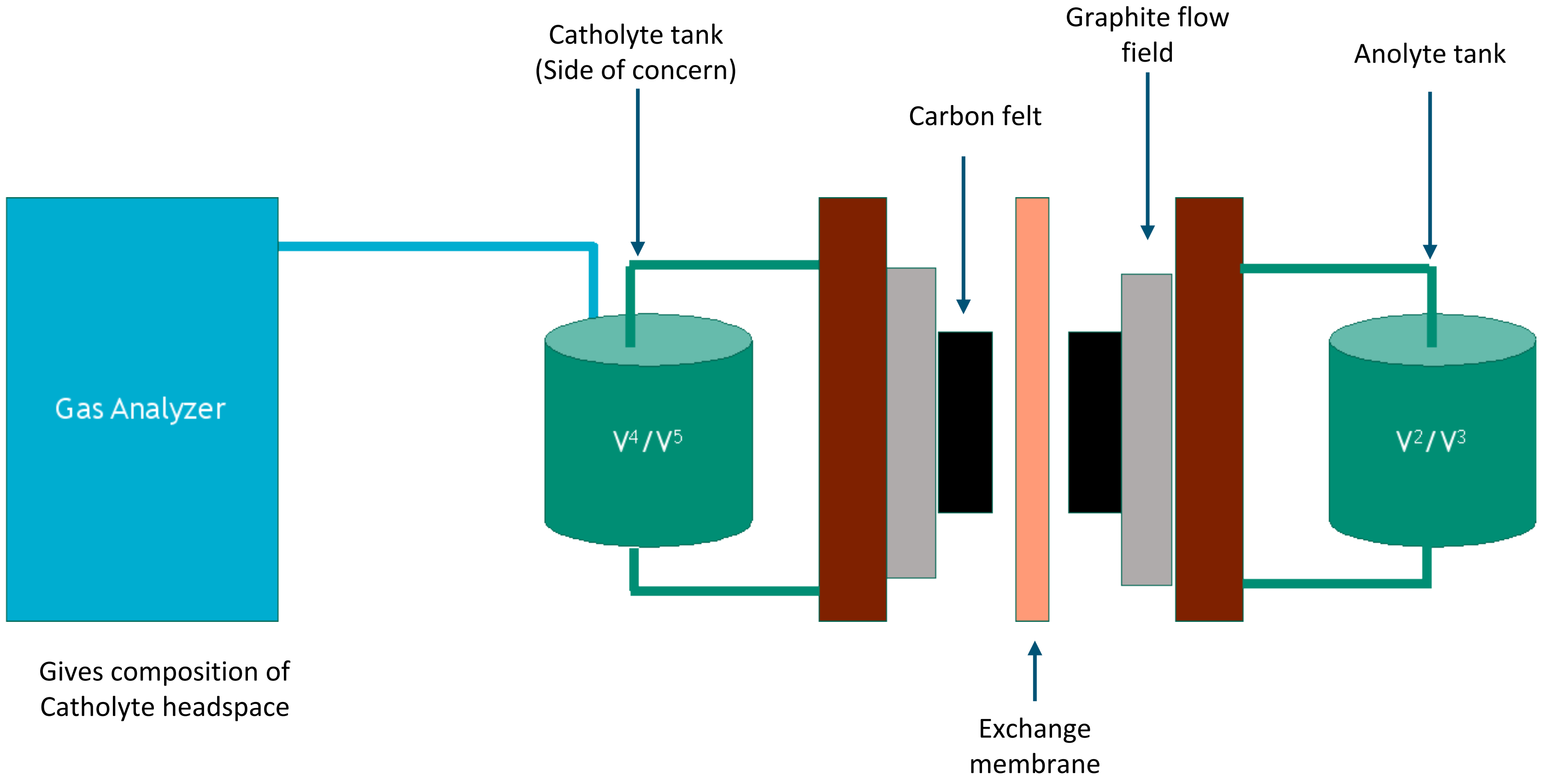


Small scale test setup

Can precisely control:

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

Directly determine what conditions cause gas evolution



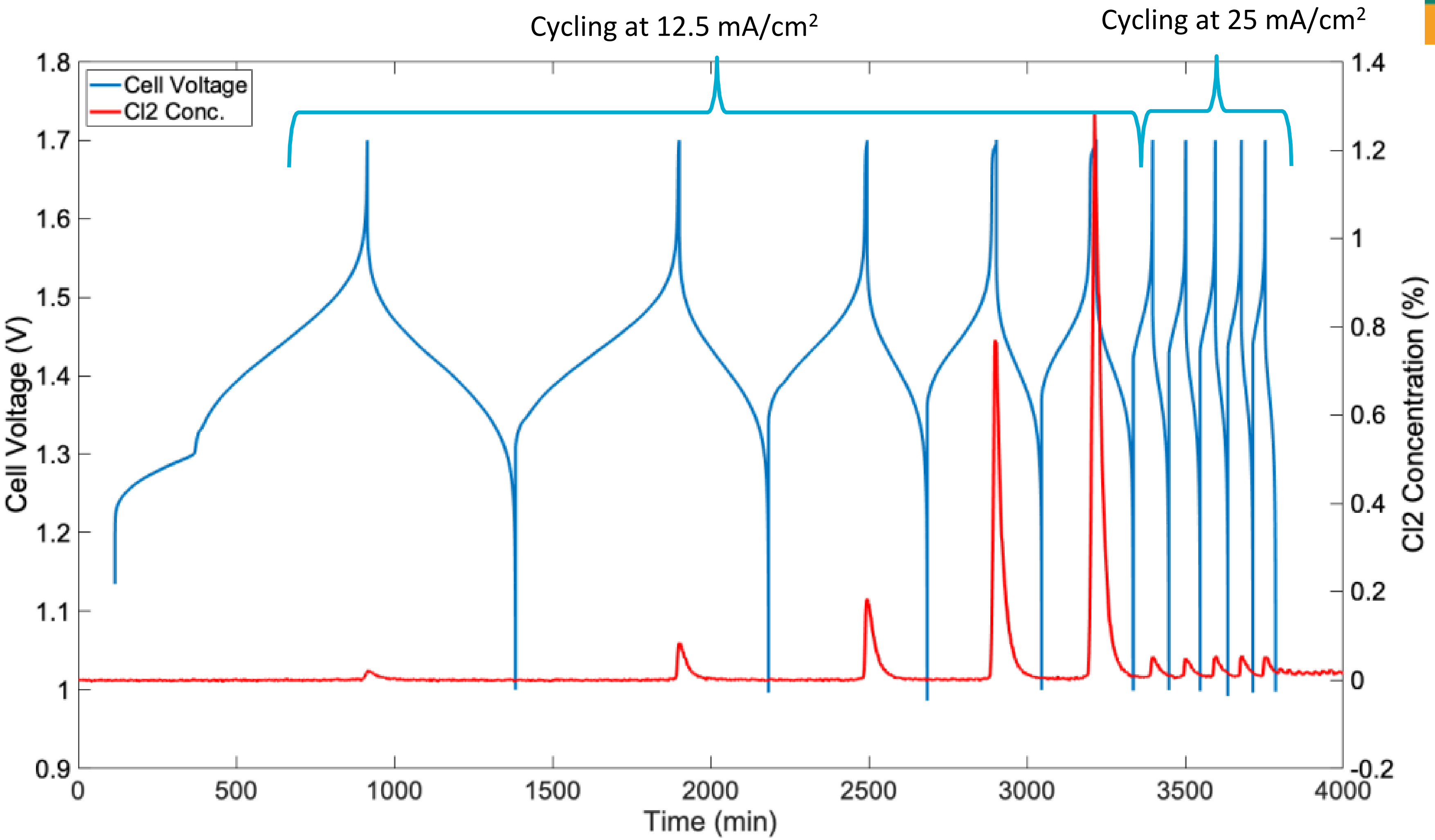
Full Cell reaction:

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

$$E = 1.26V$$

Gas evolution can occur near high charge

- Tracking Cl_2 as percent of gases sampled by UGA
  - Calculated by dividing partial pressure of Cl_2 by the total pressure of species measured
- Matching Cl_2 concentration with cell voltage during cycling
- Voltage range 1-1.7V (0-100%SOC)

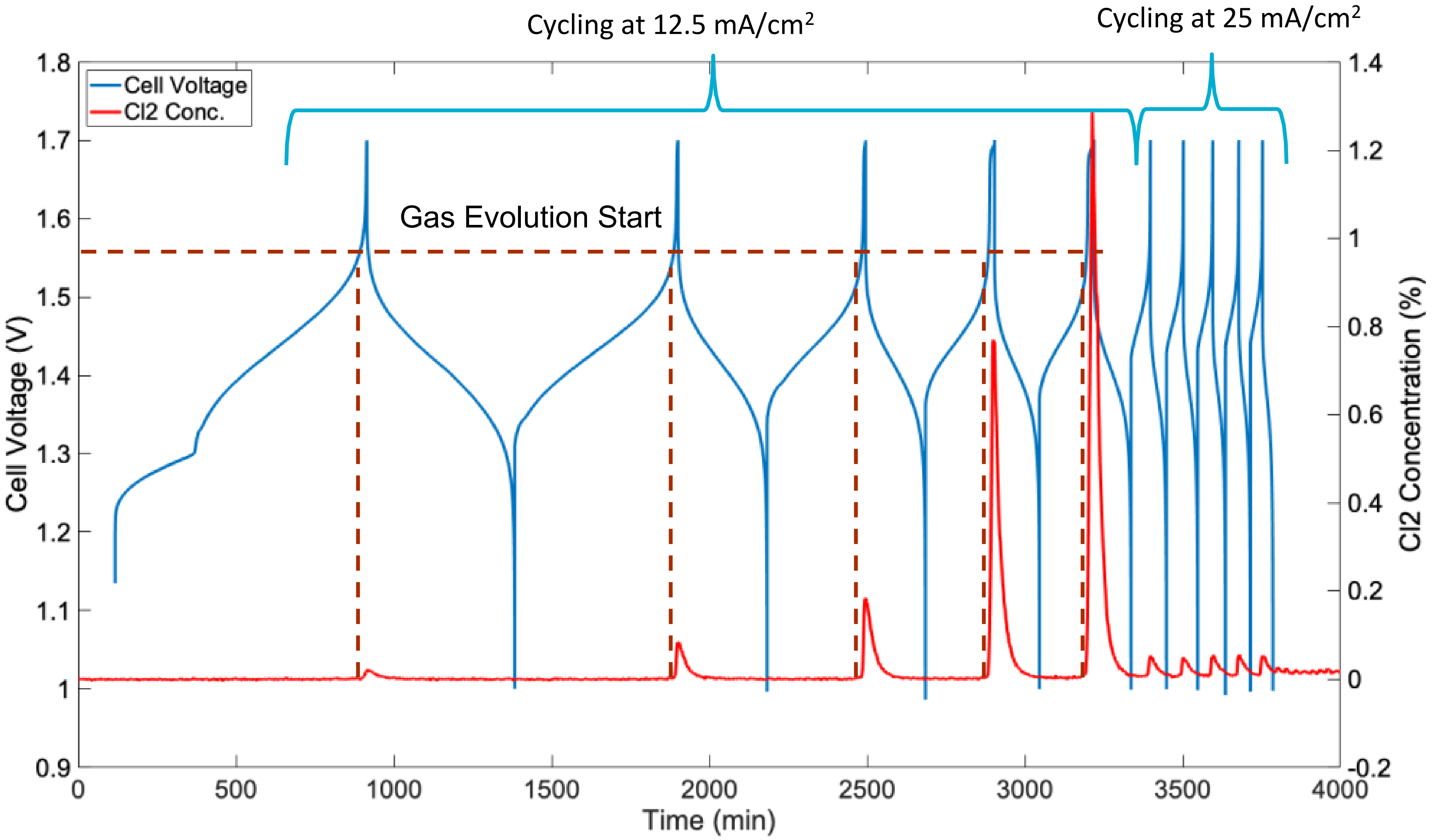


Gas evolution can occur near high charge

Total amount of gas produced at higher current densities is reduced

The cell is at high voltage for less time

This reduces the amount of time there is to produce Cl_2 gas



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

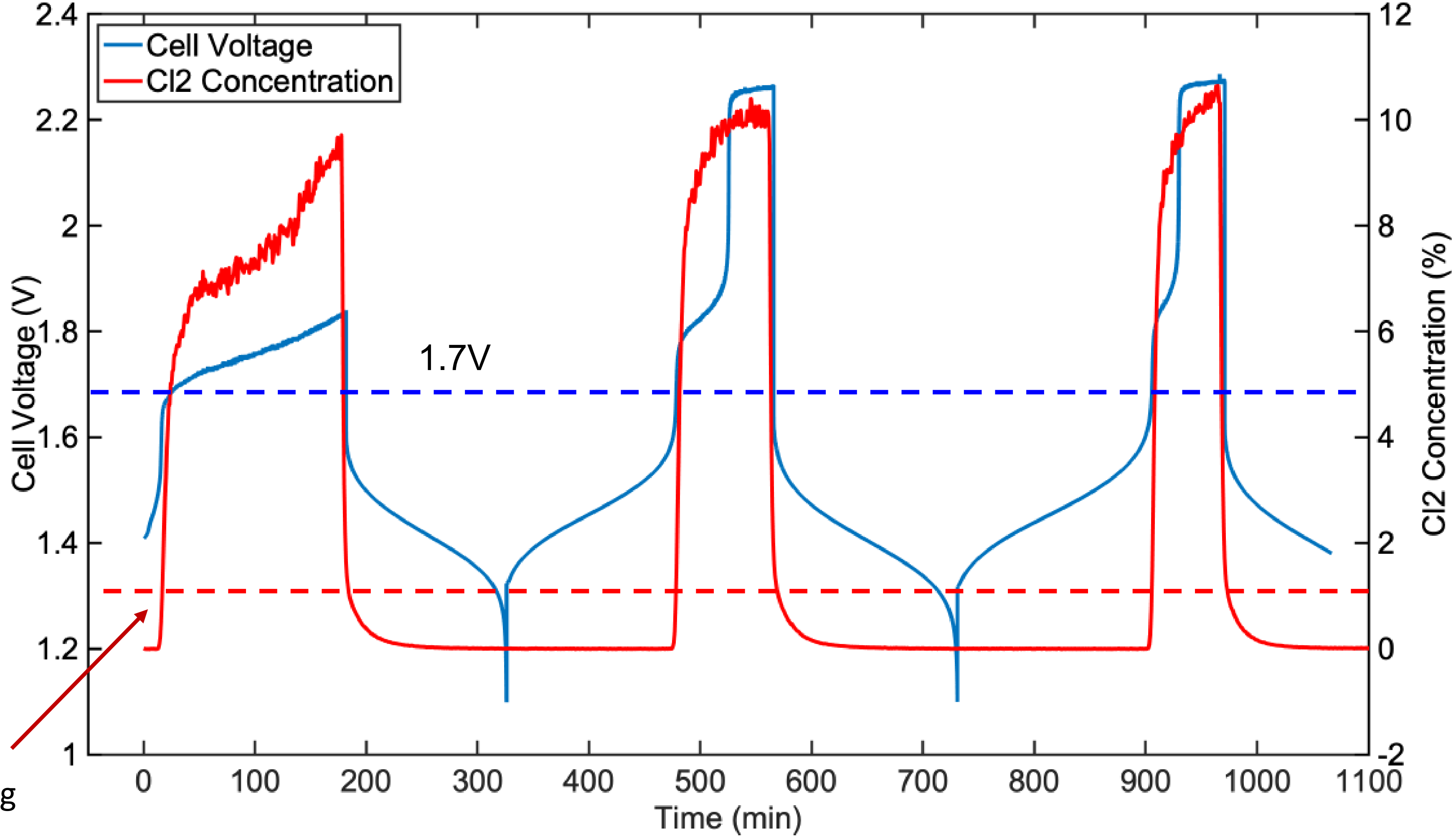
Cycling at 12.5mA/cm^2

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

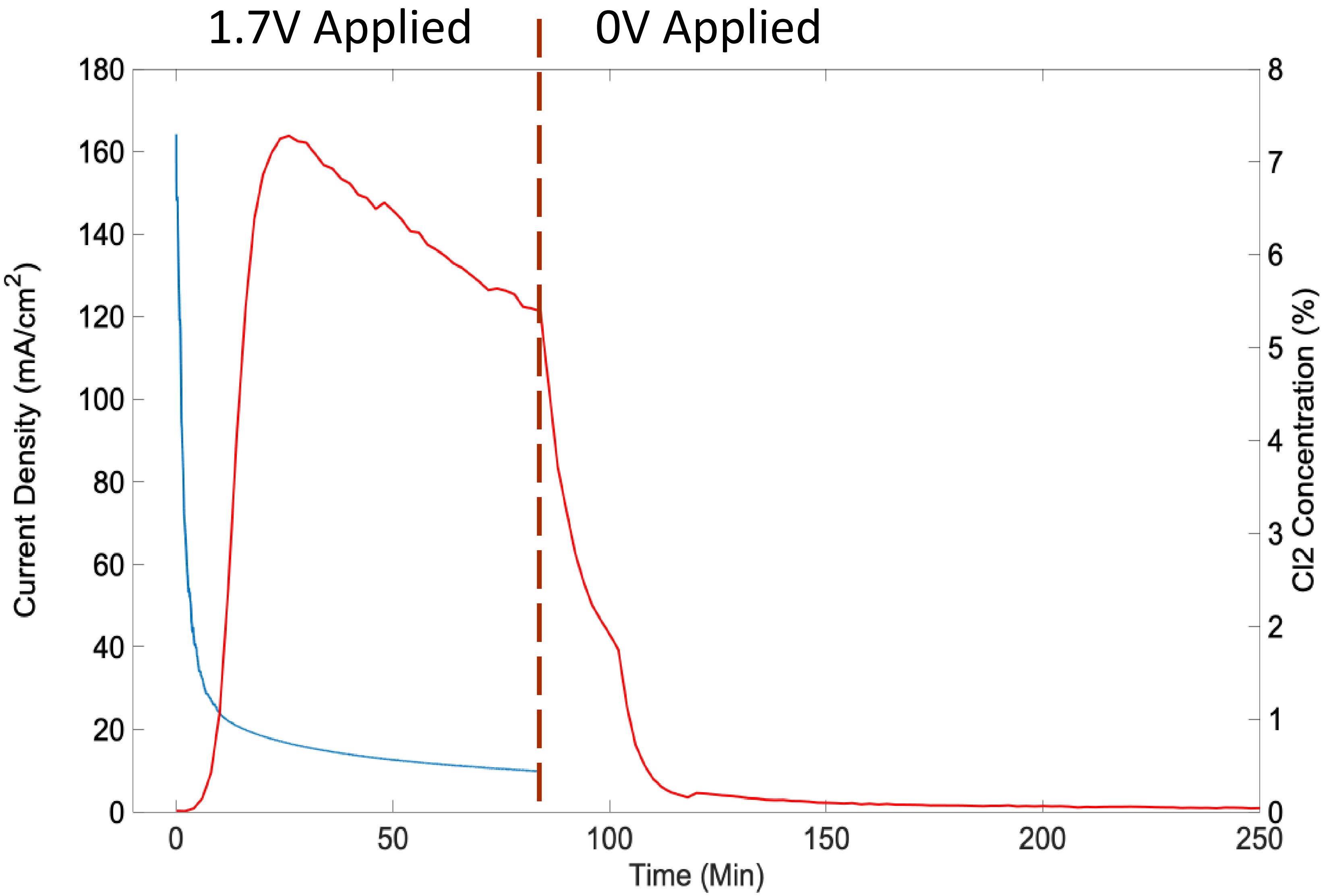
High overpotential appears to be the cause of gas evolution

Constant 1.7V applied while cell is at 100% SOC

Cl2 concentration peaks under applied voltage

After peak, Cl2 Concentration decreases

Cl2 amount decreases significantly after potential is removed



High overpotential appears to be the cause of gas evolution

Constant 1.7V applied while cell is at 100% SOC

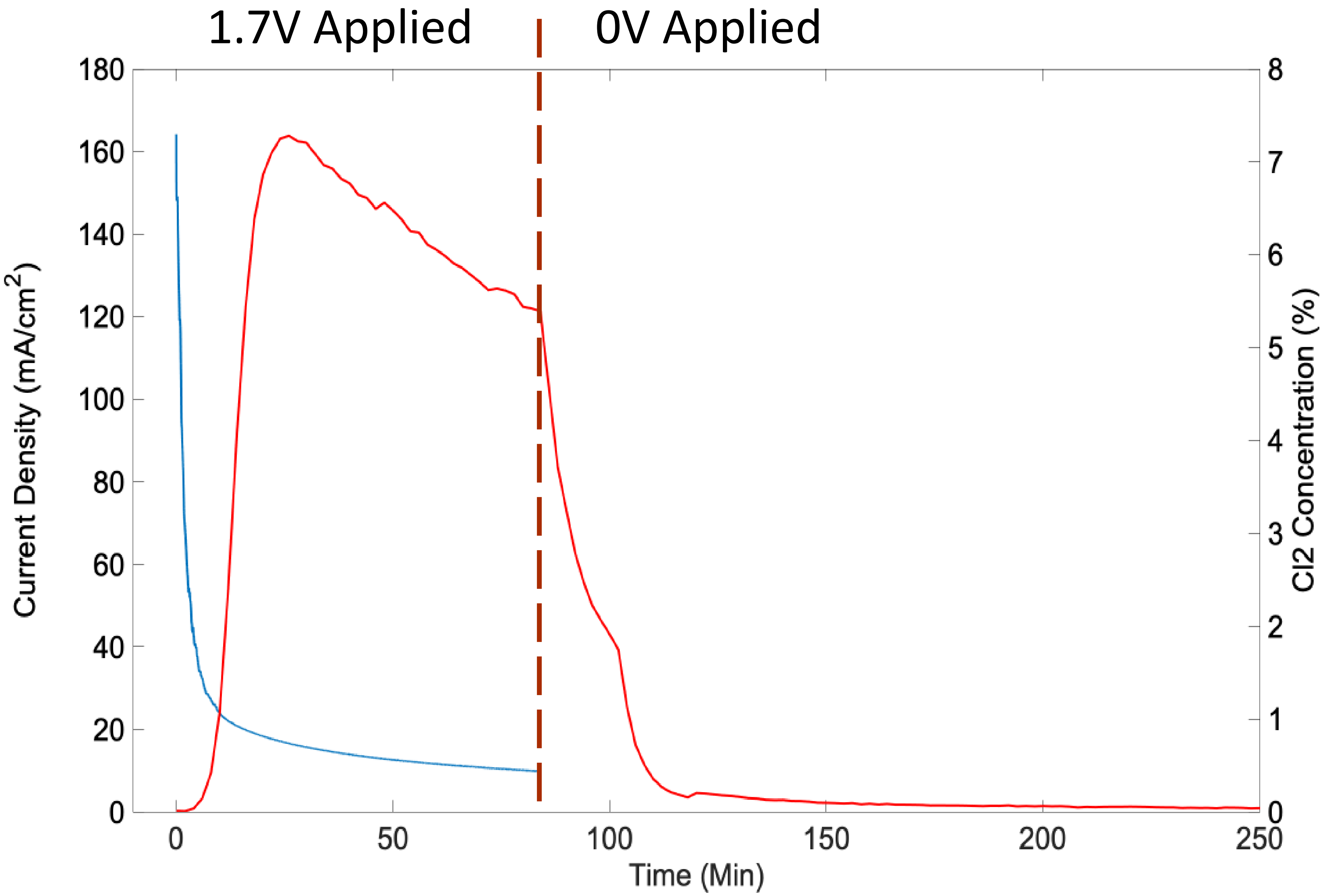
Cl2 concentration peaks under applied voltage

After peak, Cl2 Concentration decreases

Cl2 amount decreases significantly after potential is removed

High SOC without applied voltage does not induce gas evolution

Gas accumulation appears to be a function of gas generation and reabsorption by electrolyte



Cl_2 gas accumulation is governed by electrochemical generation and reabsorption into the electrolyte

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

- Cathode is at higher voltage relative to SHE than previously assumed
- Carbon electrode could be a catalyst for this reaction

Higher voltages can increase the amount of gas evolved

Cl_2 gas reaches an equilibrium as gas starts to be reabsorbed into the electrolyte

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

Initial suggestions for issue mitigation

Must note limitations of work so far

- Small scale
- Initial experiments
- More work is required to better understand phenomenon

Initial results suggest the following are viable mitigation strategies

Operational

- Limit SOC range
- Prevent high cathode potentials
  - Optimize internal resistances
  - Optimize mass transport
  - Increase catholyte volume relative to anolyte volume

Environmental

- Increase headspace of system
- Consume Cl_2 as it is generated
  - Initiate reaction with H_2 on small scale
  - Increase rate of absorption into the electrolyte

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