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Quantifying Chlorine Gas Evolution from Mixed-Acid Vanadium Redox Flow Batteries

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U.S. DEPARTMENT OF ENERGY

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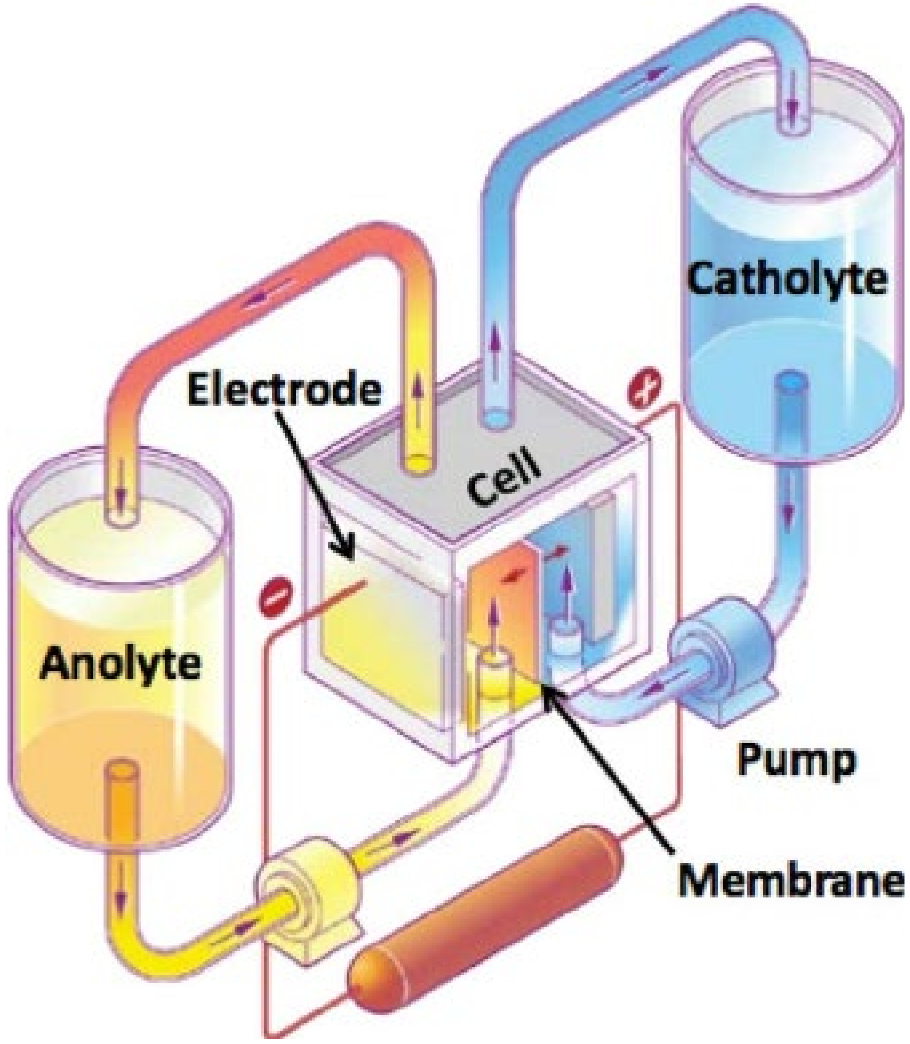
Introduction to Flow Batteries

- Charged species are dissolved into electrolyte
- Electrolyte is pumped from storage tanks to electrode stacks
- Reaction takes place in the reactor stack and products are pumped back to storage tanks

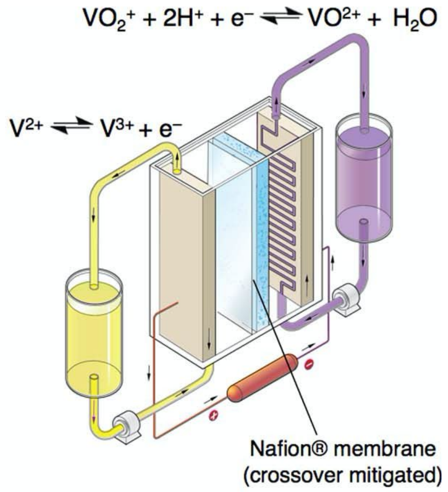


Travis Anderson, Sandia National Laboratories, 2013

Background on Flow Battery Safety

- Thermal runaway is generally not a concern
- However leaks and gas generation are issues[1]

- 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



Open Circuit Potential (OCP) **1.3 V**

Representative 2MW/8MWhr Vanadium Redox Flow battery system

[1] Wittman, R. M.; et. al. Perspective: On the Need for Reliability and Safety Studies of Grid-Scale Aqueous Batteries. J. Electrochem. Soc. 2020,167(9), 90545.
*Based on energy density of 25wh/L K. Lourenssen et al, J. Energy Storage, 25 (2019)

Background on Mixed-Acid Redox Flow Battery

- H_2SO_4 and HCl electrolyte mix
  - Increases vanadium solubility
  - Increases stable temperature window
  - Can produce significant amounts of Cl_2 gas

	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

Background on Mixed-Acid Redox Flow Battery

- H_2SO_4 and HCl electrolyte mix
  - Increases vanadium solubility
  - Increases stable temperature window
  - Can produce significant amounts of Cl_2 gas
- 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
- 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

	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

$$Cl_2 + H_2 + \text{Ignition source} \longrightarrow 2Cl^- + H_2 \longrightarrow 2HCl$$

Releases 184kJ per mole

Hypothesis: Cl_2 Gas Generation Likely Occurs Through One of These Mechanisms

Electrochemical Cl_2 production

$$eq\ 1.\ 2Cl^- \rightarrow Cl_2 + 2e^-,\ E_0 = 1.359V\ vs\ SHE\ at\ STP, 1M\ HCl$$

Chemical self discharge of posolyte that produces Cl_2

$$eq\ 2.\ VO_2^+ + 2H^+ + Cl^- \rightarrow VO^{2+} + H_2O + \frac{1}{2}Cl_2$$

Previous Work Determined Neither Reaction was Likely but Did Not Directly Observe Cl_2 Generation

Electrochemical Cl_2 production

$$eq\ 1.\ 2Cl^- \rightarrow Cl_2 + 2e^-\ ,\ E_0 = 1.359V\ vs\ SHE\ at\ STP, 1M\ HCl$$

- Potential is ~360mV above V^{4+}/V^{5+} charging reaction potential of 1V vs SHE and was ruled out

Chemical self discharge of posolyte that produces Cl_2

$$eq\ 2.\ \ VO_2^+ + 2H^+ + Cl^- \rightarrow VO^{2+} + H_2O + \frac{1}{2}Cl_2$$

- Analysis found that this reaction is thermodynamically run in reverse and consume Cl_2

Cl_2 gas generation was never measured directly rather observed through indirect methods like a pressure plate

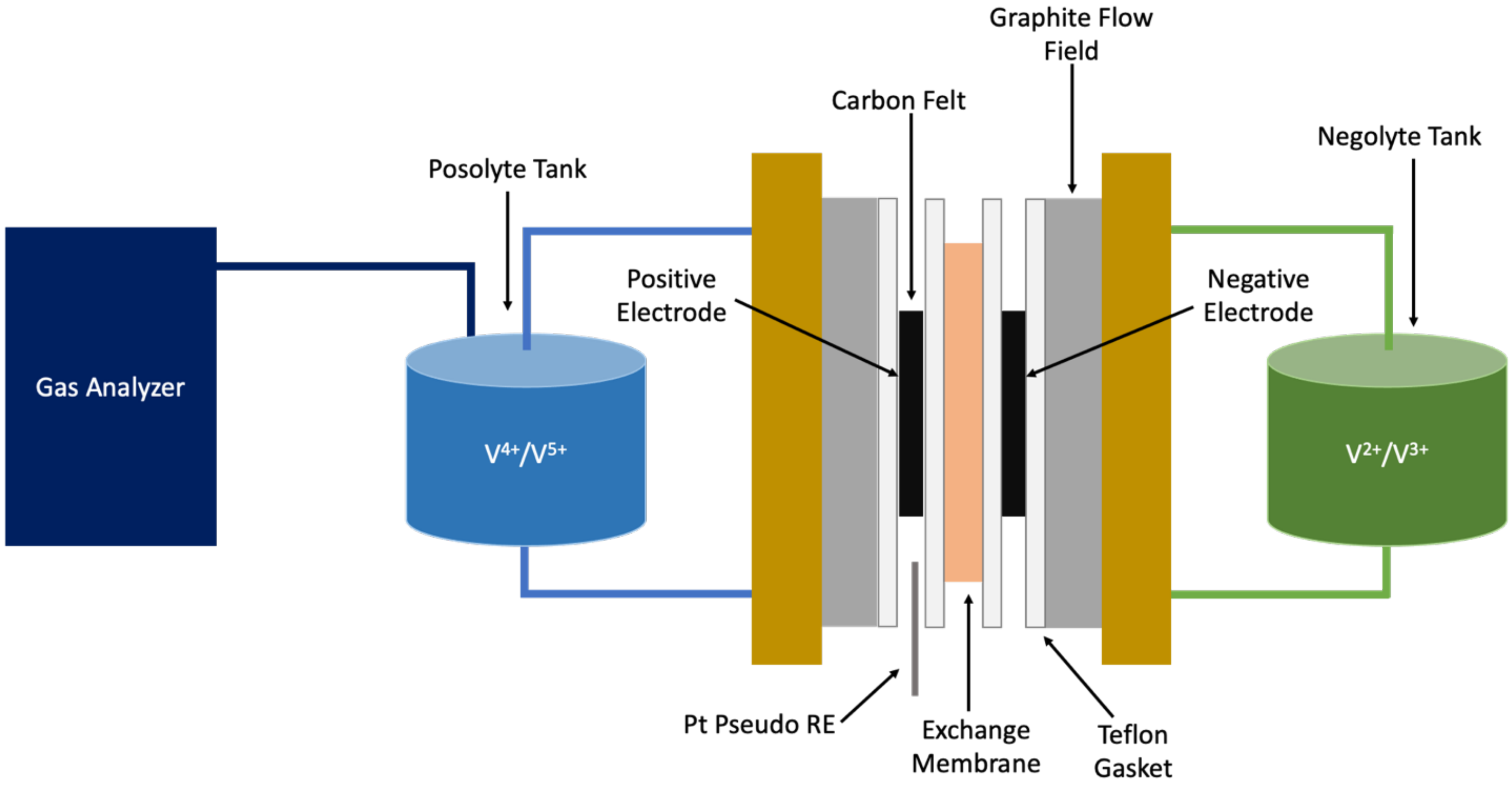
Key Objectives Aligning with OE's Core Mission

- Conduct in depth research and analysis to:
  - Determine the mechanism of Cl_2 gas generation during cycling of a MA flow battery
  - Quantify how much gas is formed under various conditions
- Estimate how much gas could be generated in a large grid-connected system to determine the scope of of a potential problem in the field and prepare for potential incidents
- Propose ways Cl_2 generation can be avoided or how the hazard can be mitigated to enable the utilization of MA VRFBs for a more resilient and flexible grid

Small Scale Test Setup

Key Innovations:

- First time Cl_2 gas generation is directly observed in a mixed acid flow battery in a public study
- Use of a reference electrode which is uncommon in flow battery research



Experimental:

- Electrode: 5cm^2 graphite based felt
- Reference electrode: Pt Wire
- Electrolyte: 20ml each side 2M VSO4 + 5MHCl
- Gas Measuring system: UGA 200 Gas Analyzer

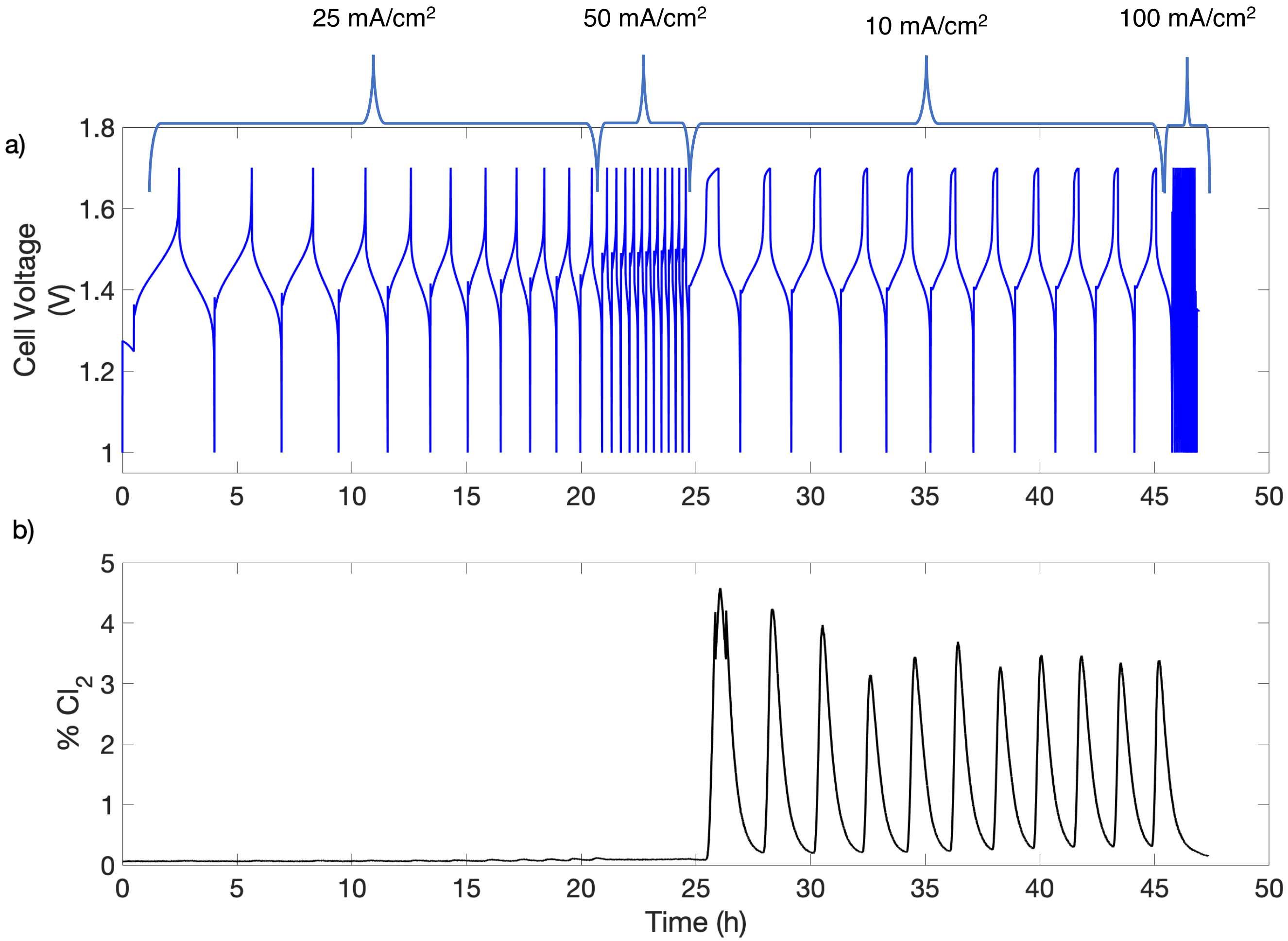
Full Cell reaction:

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

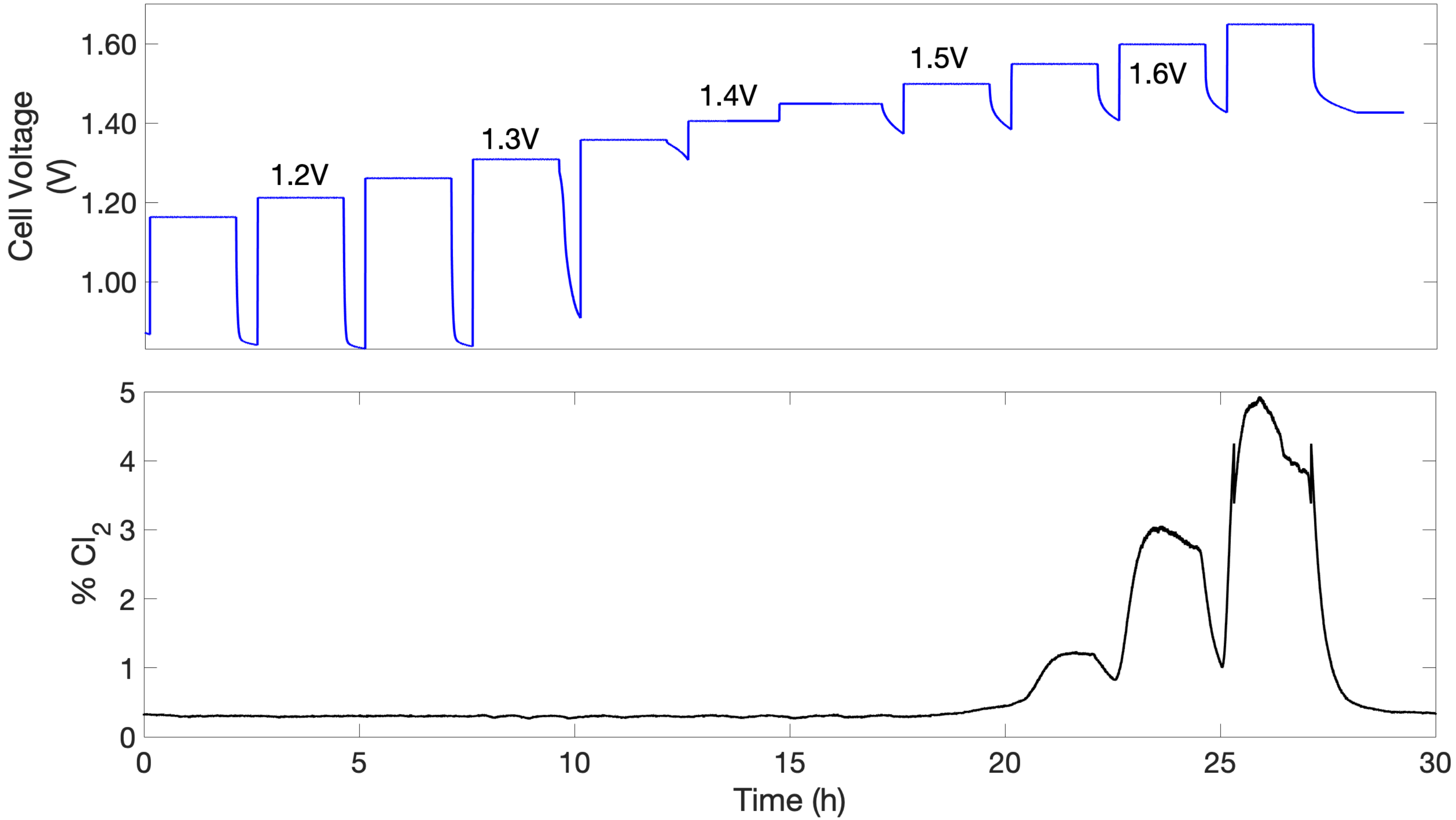
$$E = 1.26V$$

Results: Observe Cl_2 Generation at High States of Charge

- 4% Cl_2 observed at low current density cycling (10 mA/cm^2)
- Gas generation may be tied to time above a critical voltage
- Gas levels decrease rapidly when battery is discharged suggesting Cl_2 can be consumed by the electrolyte easily



Results: Potential Step Experiment Confirms Electrochemical Mechanism for Cl_2 Generation

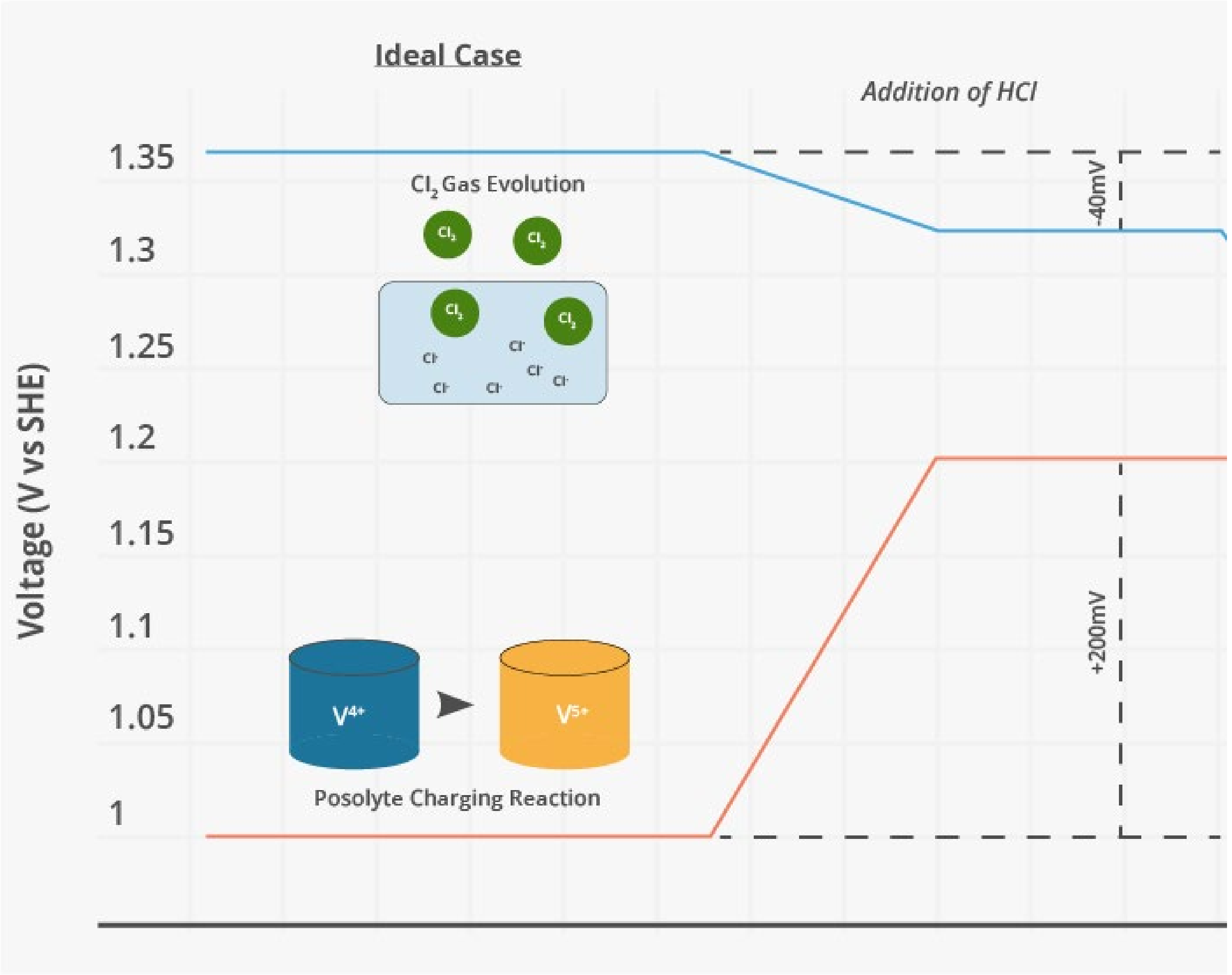


- When potential is removed, the gas concentration drops rapidly indicating that Cl_2 is generated when potential is applied and current is being passed through the cell

Results: There are a Number of Small Factors that Build to Enable Gas Evolution

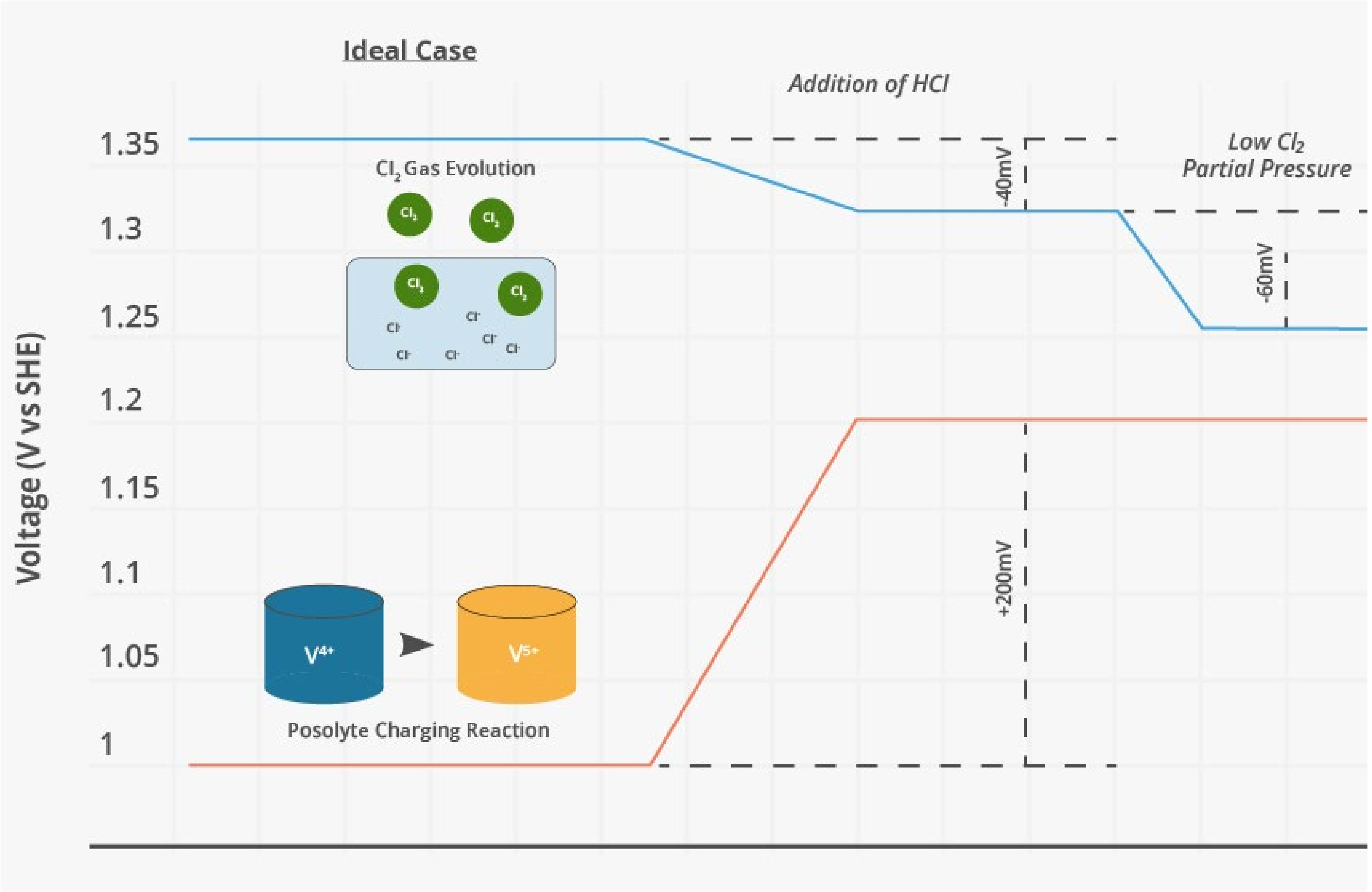
- Based solely on the ideal case, Cl_2 generation should not occur through an electrochemical pathway
  - $2Cl^-/Cl_2$ formal potential is 1.359 V vs SHE
  - V^{4+}/V^{5+} formal potential is 1.00 V vs SHE
- This 359 mV potential difference should be enough to prevent gas generation even in a very inefficient battery

Results: There are a Number of Small Factors that Build to Enable Gas Evolution



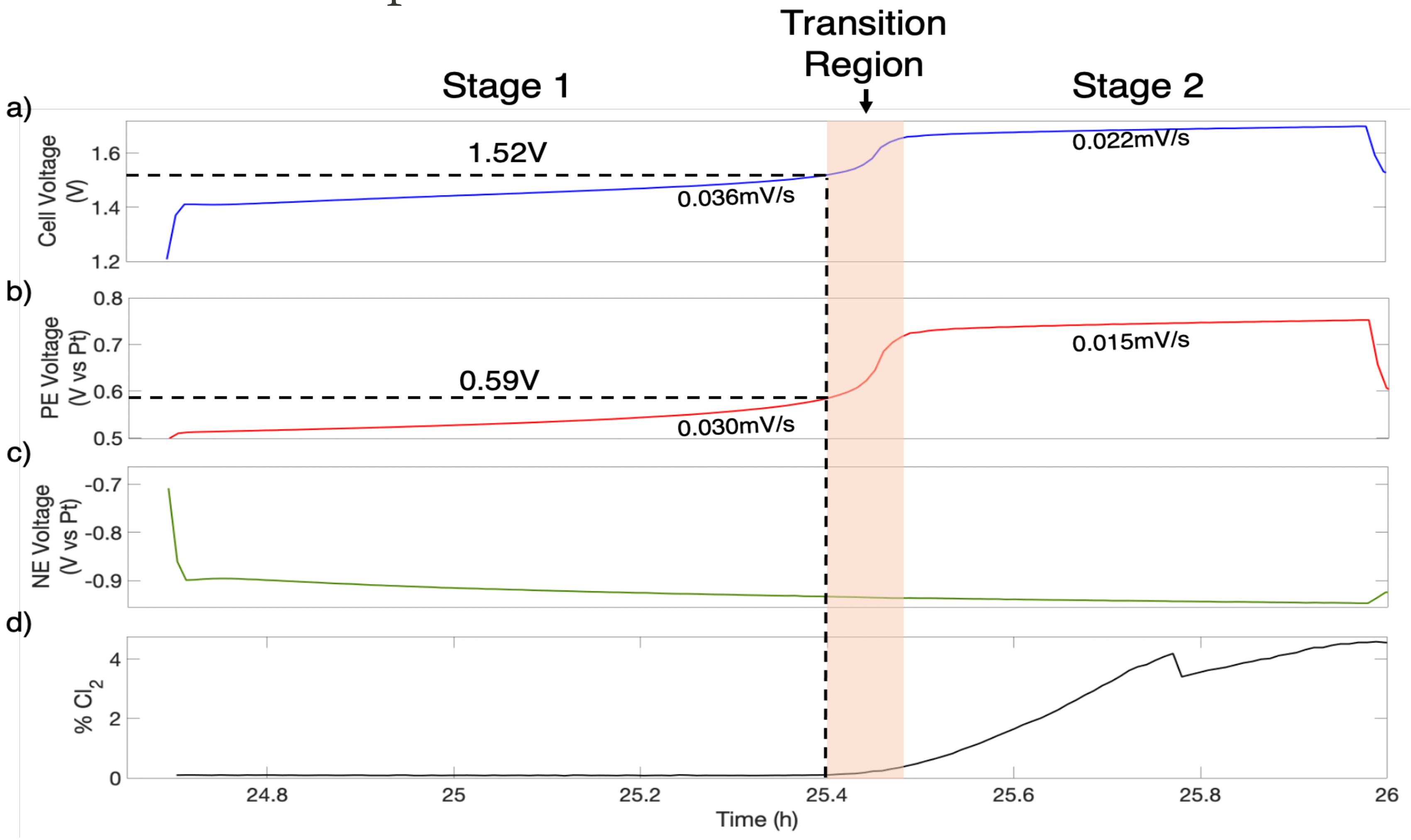
- At 5M HCl the $2Cl^-/Cl_2$ formal potential is decreased by ~40 mV
- Previous work on MA system shows that the V^{4+}/V^{5+} formal potential is increased by about 200 mV

Results: There are a Number of Small Factors that Build to Enable Gas Evolution



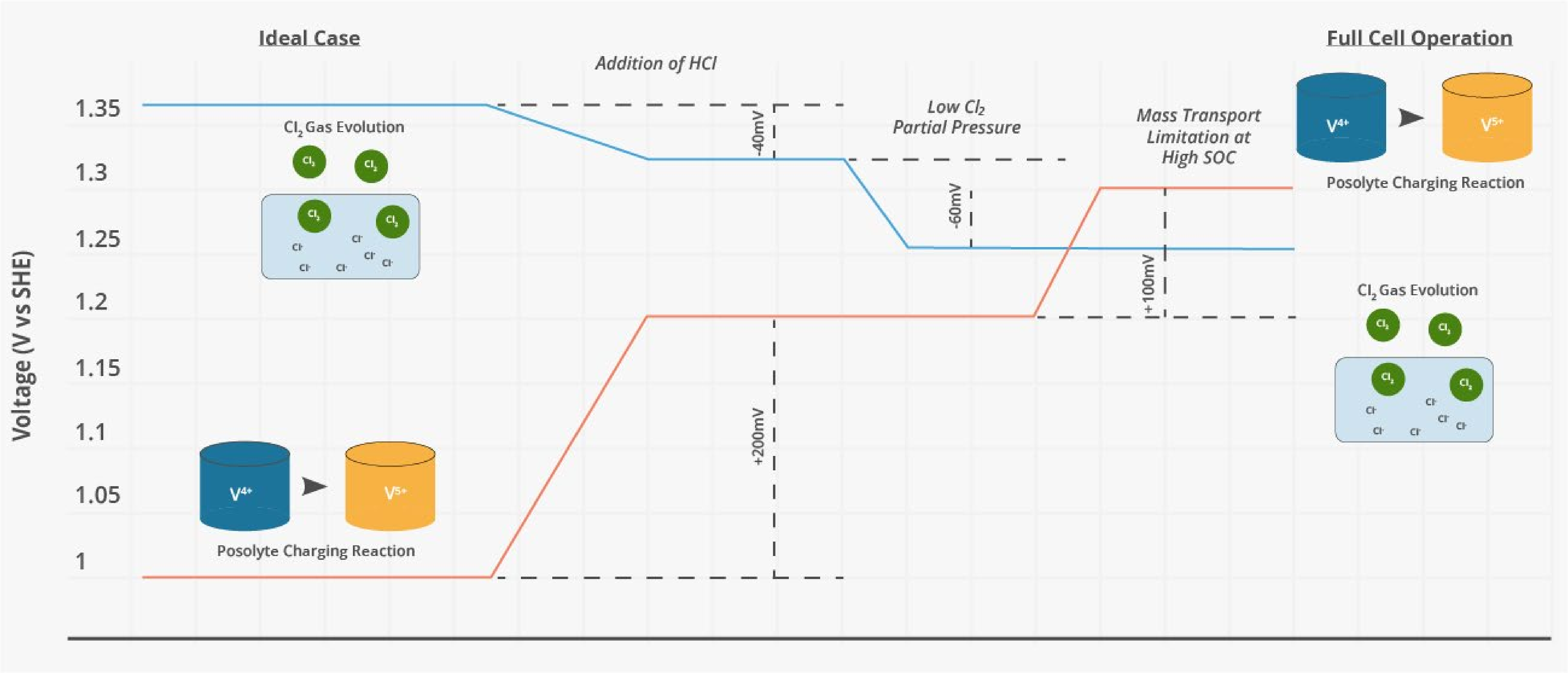
- Low partial pressure of Cl_2 above the posolyte decreases the $2Cl^-/Cl_2$ formal potential by another ~60 mV

Results: Cl_2 Gas Generation Occurs When the Positive Electrode Becomes Mass Transport Limited



Vanadium oxidation dominant during Stage 1 and Cl- oxidation dominant during Stage 2

Results: There are a Number of Small Factors that Build to Enable Gas Evolution



- Polarization of the PE by mass transport limitations at high states of charge adds 100 mV or more to the PE voltage

Impact: Estimation of Gas Generation for a Theoretical 1MW/4MWh system Indicates Cl_2 is a Significant Hazard

System Voltage	Observed % Cl_2	Total Posolyte Volume (L)	Posolyte Headspace Volume (L)	Volume of Cl_2 Generated (L)	Mass of Cl_2 at STP (g)	Mole of Cl_2 (mol)	Energy Released (MJ)
1.55 V	1.2	115,000L	11,500	140	437.4	6	1.1
1.65 V	4.9	115,000L	11,500	564	1,679.8	25.2	4.6

Assumptions:

- Gas generation will be limited to a percent of the posolyte headspace at a given potential
- Use observed % Cl_2 from lab-scale system
- Headspace is 10% of the posolyte volume

Impact: Initial Suggestions for Hazard Mitigation to Enable Adoption of MA VRFBs

Initial results suggest the following are viable mitigation strategies:

Operational

- Limit SOC range to max 75%
- Prevent high cathode potentials
  - Optimize internal resistances
  - Optimize mass transport
  - Increase catholyte volume relative to anolyte volume

Environmental

- Decrease 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

Conclusions

- Cl_2 gas evolution occurs through an electrochemical mechanism enabled by a number of small influences adding up
  - Addition of HCl
  - High HCl concentration and low Cl_2 partial pressure
  - Mass transport limited PE at high states of charge
- Amount of Cl_2 gas generated would be a significant safety hazard for a fielded system and needs to be addressed with appropriate controls in future deployments
- Systematic research should be conducted to study potential safety and reliability issues of ABs to prevent future incidents with emerging technologies

Full study covered in submitted manuscript: *Reed M. Wittman , Cassandria Poirier, Harry D. Pratt III, Travis M. Anderson, Yuliya Preger,* "Quantification of Chlorine Gas Generation in Mixed-Acid Vanadium Redox Flow Batteries"

Preprint available at ECSarXiv: https://ecsarxiv.org/un3p7/

Other Work in the Aqueous Battery Safety and Reliability Portfolio

- Life time prediction of $Zn\text{-}MnO_2$ batteries for NTUA off-grid solar plus storage deployment (See poster by Henry Guan "Off-Grid Application of Zinc Manganese Dioxide Battery Energy Storage System on the Navajo Nation" for more)
- Beginning the process of testing a modular mixed acid flow battery at the SNL Energy Storage Test Pad to probe how gas generation scales with real world systems.
- Developing capabilities to conduct safety and abuse testing of aqueous flow and non-flow batteries at SNL

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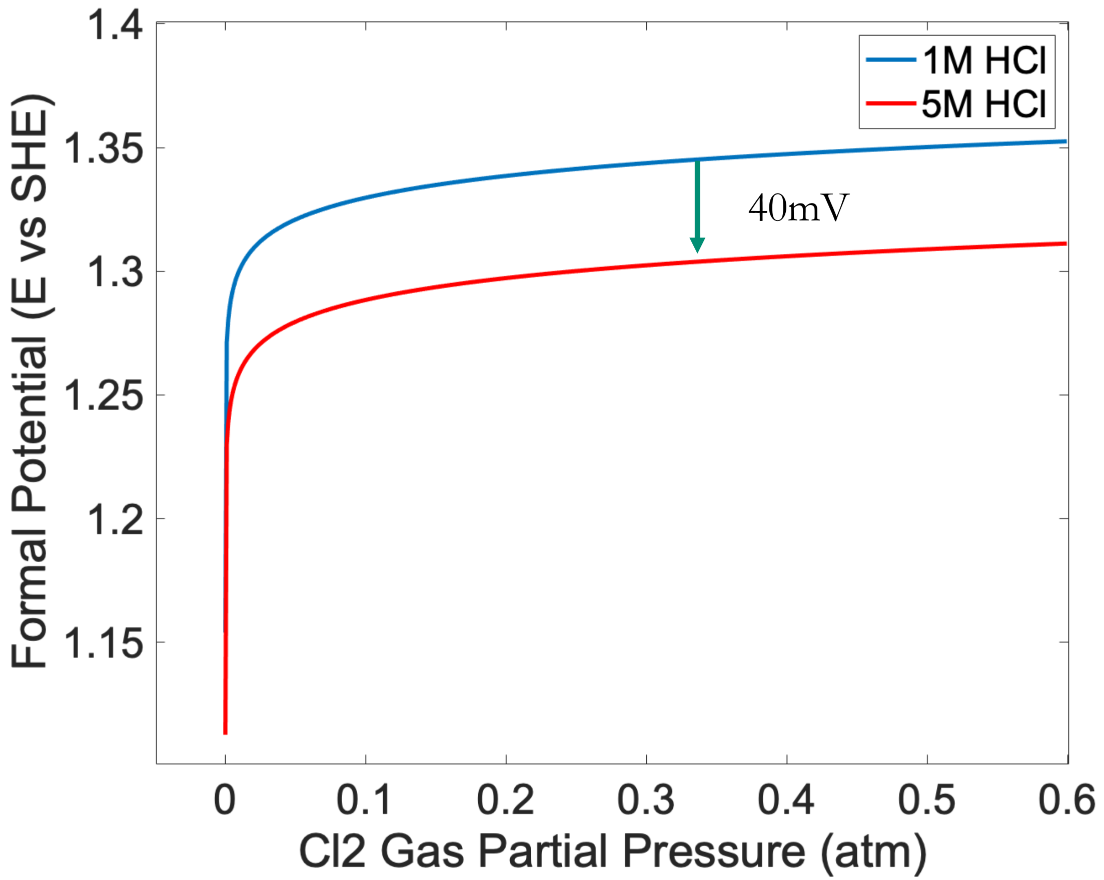
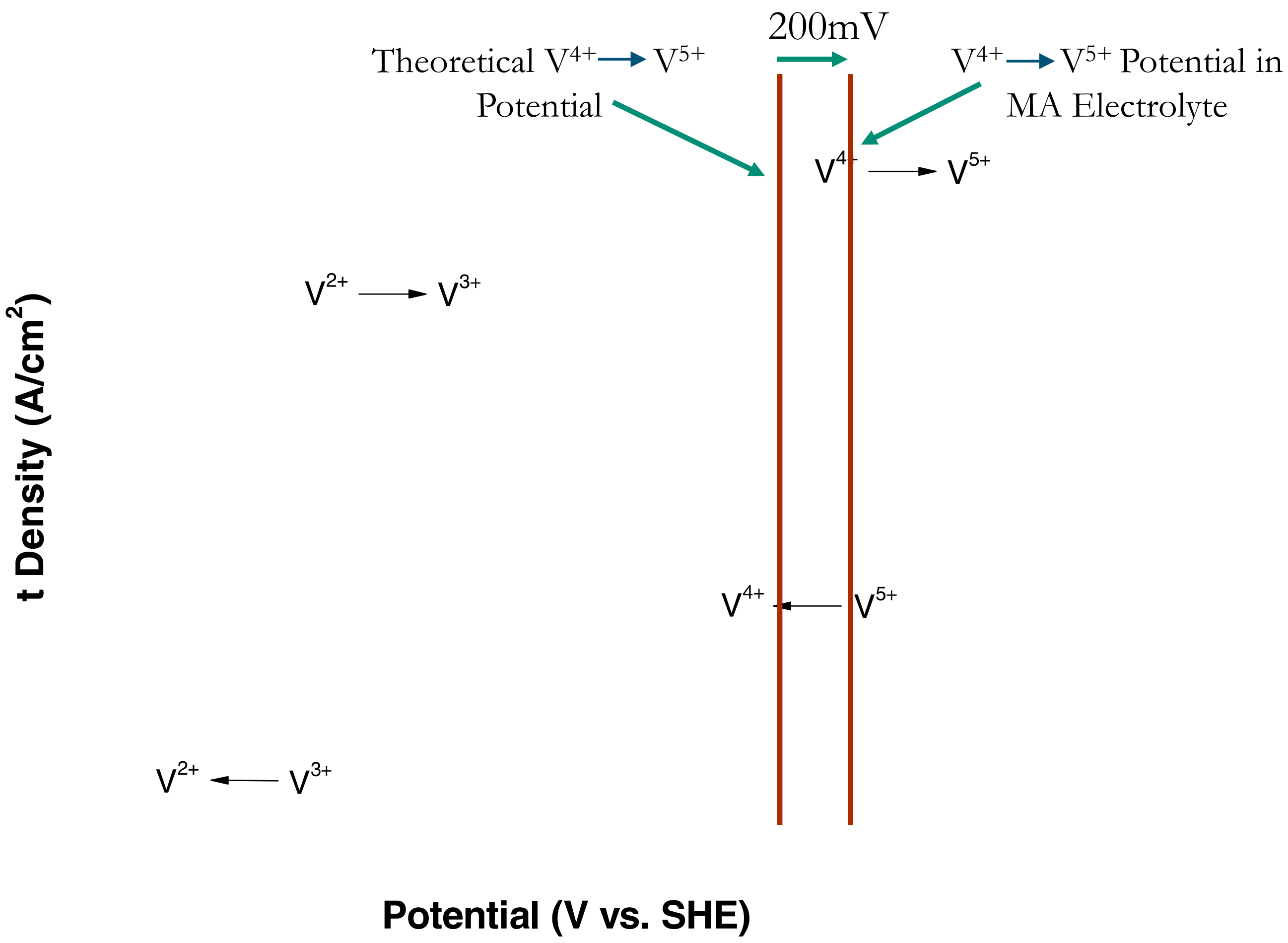
Supplemental Slides

Influence of Electrolyte Chemistry on Cl_2 Evolution and Posolyte Charging Reactions

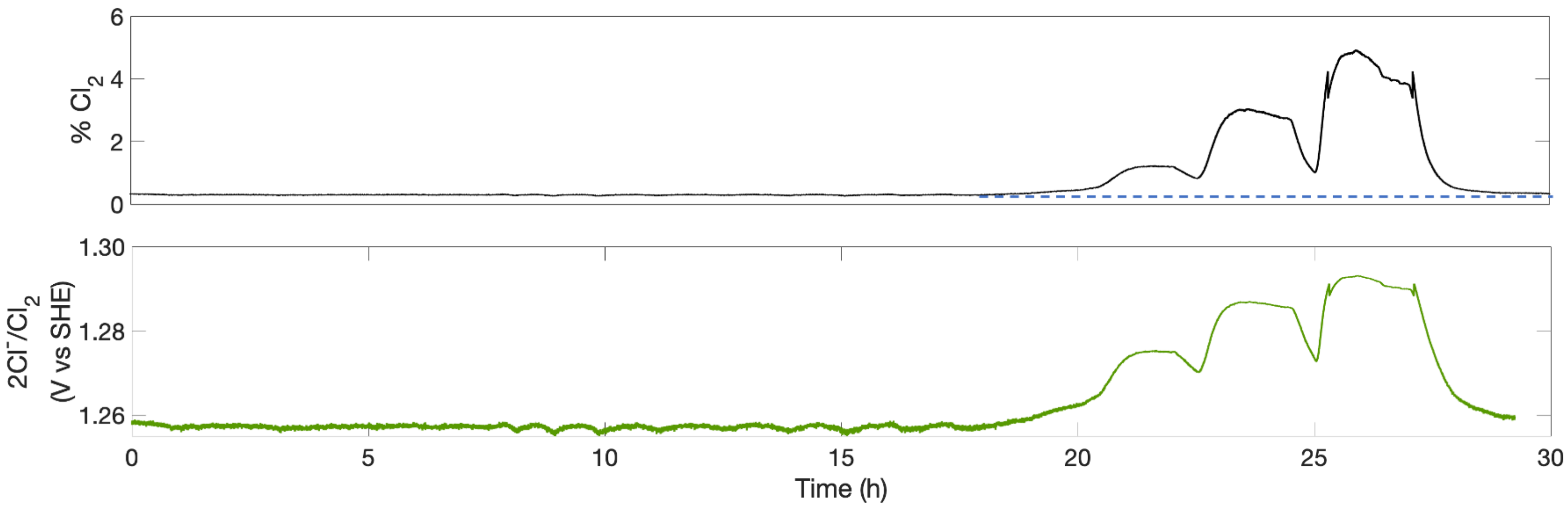
Influence of HCl Concentration and Cl_2 gas partial pressure on $2Cl^-/Cl_2$ formal potential





Li et al., Adv. Energy Mater. **2011**, *1*, 394–400

Influence of Low Partial Pressure on Cl_2 Evolution Reaction



Relationship between Cl_2 partial pressure and Cl_2 evolution is given by:

$$E^0 = 1.359 + 0.0295 log\left(\frac{P_{Cl_2}}{(Cl^-)^2}\right)$$

We see that at near 0% Cl_2 voltage to generate Cl_2 gas is ~1.26V vs SHE

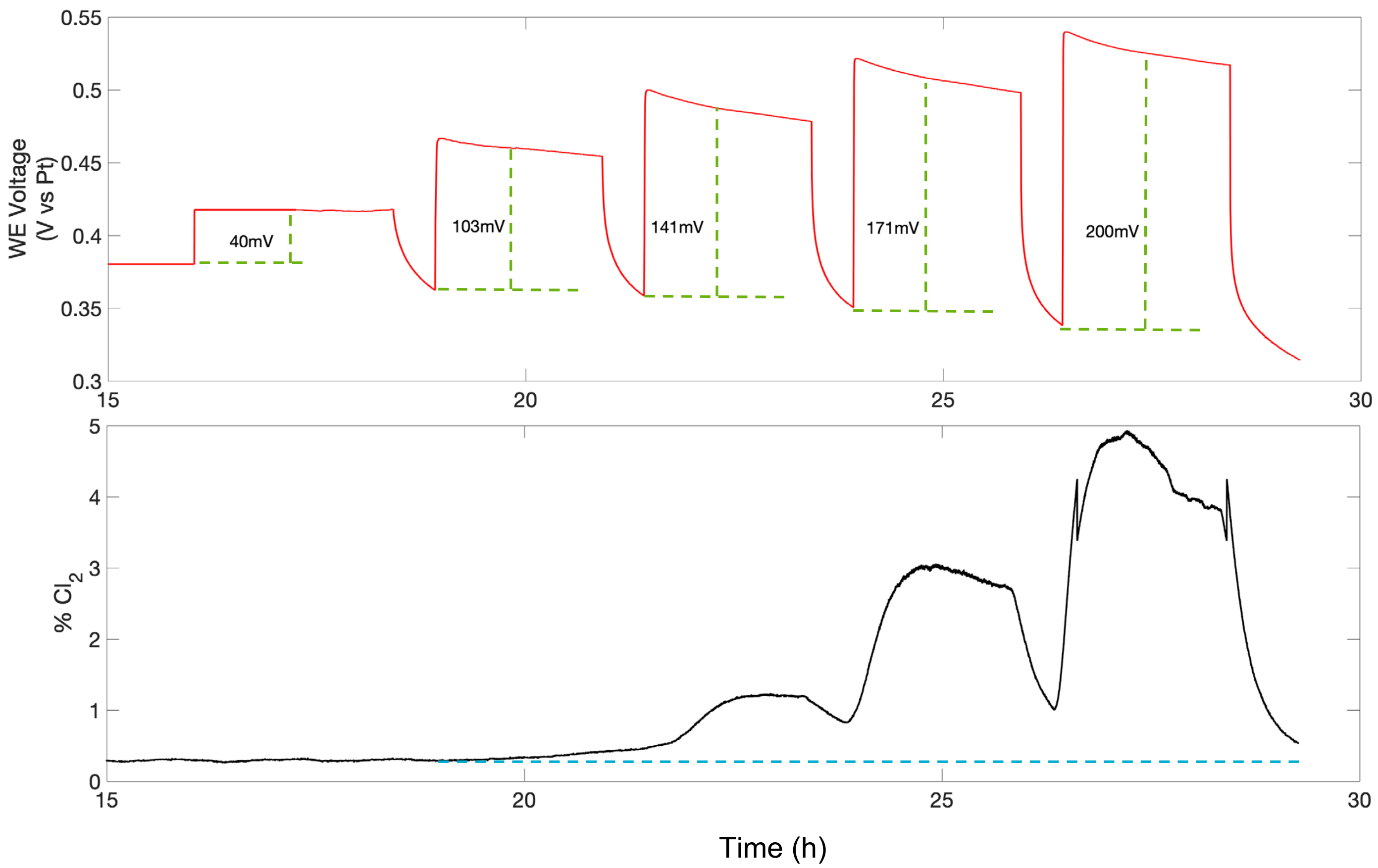
As %Cl_2 increases so does the voltage evolve Cl_2 but always stays below 1.3V vs SHE

100mV of PE Polarization from Mass Transport Limitations Appears to be the Threshold to Generate Cl_2 Gas

When the polarization of the PE is less than 100mV we do not see any gas generation

When it is equal to or larger than 100mV we start to see gas generate

Additional increases in polarization of the PE increases the amount of Cl_2 generated



Governing Equations

$eq\ 3.\ VO_2^+ + 2H^+ + e^- => VO^{2+} + H_2O\ , E_o = +1.00V\ vs\ SHE$ Charging reaction in posolyte

$eq\ 4.\ \log(Cl_2) = -1.21 + \log(P_{Cl_2})$ Cl_2 reabsorption reaction