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Quantification of Chlorine Gas Generation in Mixed-Acid Vanadium Redox Flow Batteries

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Introduction:

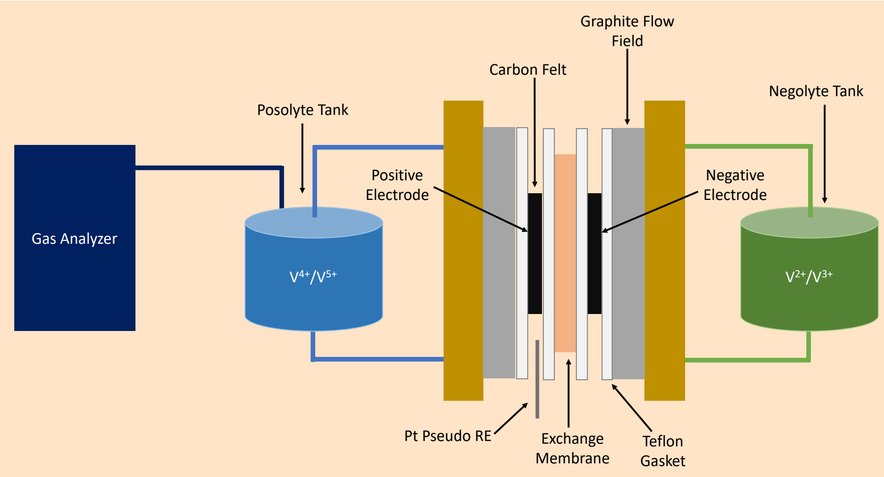
- Mixed Acid Vanadium Electrolyte is composed of H_2SO_4 and HCl
  - Increases vanadium solubility
  - Increases stable temperature window
  - Can produce significant amounts of Cl2 gas
- Cl2 gas is a safety hazard to people and environment
- Max 60min dose is 3ppm
- Cl2 plus H2 is an explosive mix
- Fielded systems have had issues with Cl2 generation
- Cl2 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

Methods:

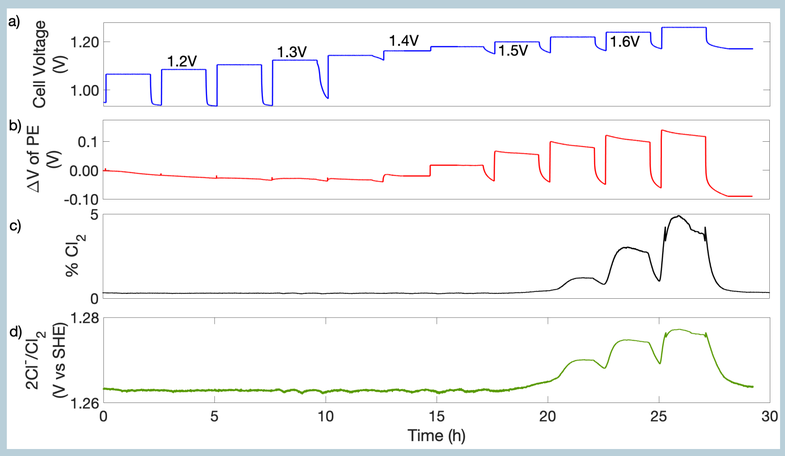
- Electrode: 5cm2 graphite based felt
- Reference electrode: Pt Wire
- Electrolyte: 20ml each side 2M VSO4 + 5MHCl
- Gas Measuring system: UGA 200 Gas Analyzer

- Key Innovations:
  - First time Cl2 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



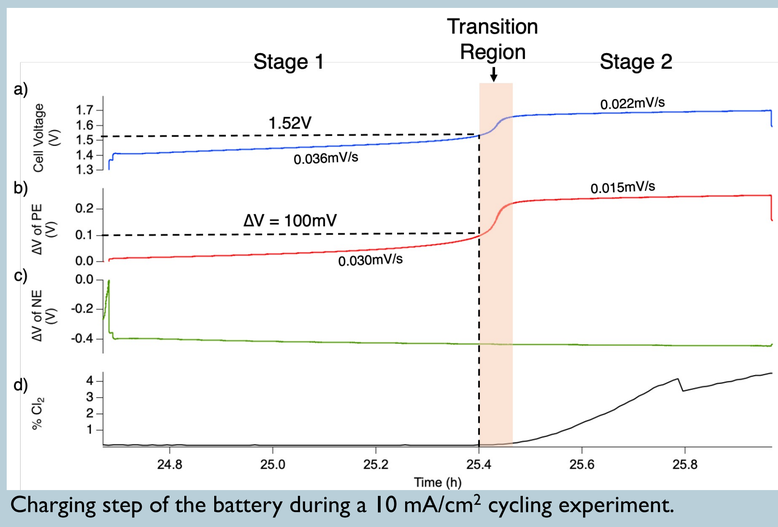
Results:

- When potential is removed, the gas concentration drops
- Indicates that Cl_2 generation is tied to the application of voltage and current
- We can conclude gas generation occurs through an electrochemical pathway



Potential stepping experiment where potential was held for 2 h with a 30 min rest afterwards.
a) Cell voltage during potential steps. b) Change in PE voltage from the start of the experiment, determined by a Pt pseudo reference electrode. c) Cl2 gas concentration in the posolyte vial headspace. d) 2Cl-/Cl2 formal potential calculated using equations 4 and 5.

- During charging we we see two stages in the cell voltage
- Stage 1 is dominated by vanadium oxidation
- In the transition region the cell voltage and the positive electrode voltage increase significantly
- This coincides with the onset of Cl_2 generation
- Stage 2 appears to be dominated by Cl- oxidation



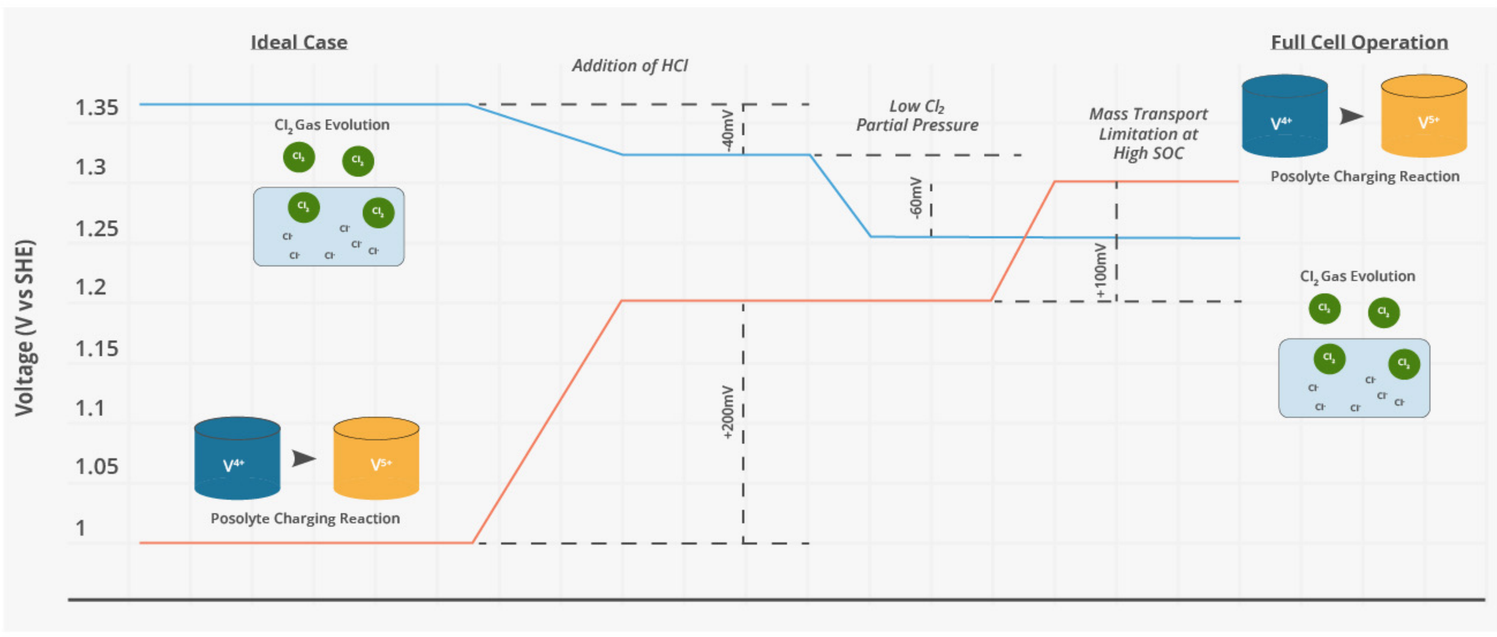
Charging step of the battery during a 10 mA/cm² cycling experiment.

a) Cell voltage. b) Change in the positive electrode voltage from the start of the experiment as determined by a Pt pseudo reference electrode (RE). c) Change in the negative electrode voltage from the start of the experiment as determined by a Pt pseudo reference electrode. d) Cl_2 gas concentration in the posolyte vial.

Discussion:

A number of factors combine to enable Cl_2 gas generation:

- The addition of HCl
  - reduces the gas evolution potential threshold
  - Increase the nominal voltage of the vanadium charging
- Low Cl_2 Partial pressure
  - Gas generation potential is dependent on Cl_2 partial pressure above the electrolyte
  - At low partial pressure the voltage to evolve gas is reduced
- During charging the positive side becomes mass transport limited
  - At higher states of charge the amount of V^{4+} that can be converted to V^{5+} trends to zero
  - To provide the required current voltage increases until it enables a new reaction
  - This reaction appears to be Cl_2 generation



Process whereby Cl_2 gas generation may become favorable in the mixed-acid vanadium flow battery. The changes to both reactions' potentials are relative.

Conclusion

- A number of factors combine to enable Cl_2 gas generation
- Gas generation occurs during cell charging at high voltages
- Amount of Cl2 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 can be found at: *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" *ACS Appl. Energy Mater.* 2023, 6, 6, 3167–3172

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