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Investigation of Hydrogen Evolution at Negative Electrode for a Vanadium Redox Flow Battery

X. Gao, M. J. Leahy and D. N. Buckley

Department of Physics
Charles Parson Initiative on Energy (CPI)
University of Limerick, Ireland

cpi Energy & Sustainable Environment

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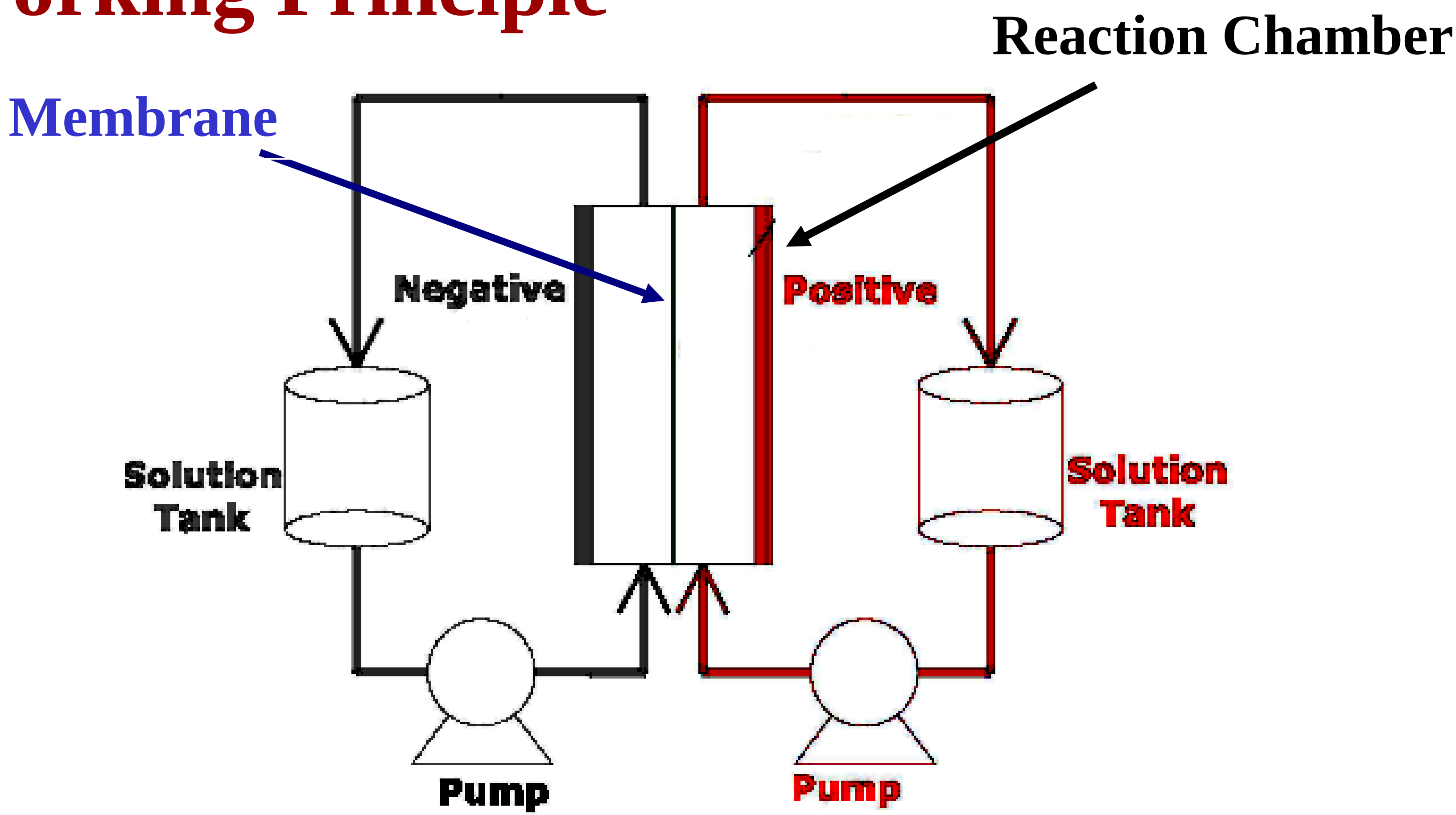
NDP NATIONAL DEVELOPMENT PLAN

Outline

- **Introduction**
- **Experimental**
  - **Charging and Discharging Battery**
    - **Two Features**
  - **Hydrogen Evolution during Preparation of Anolyte**
    - **Intermediate Specie and Possible Mechanism**
  - **Spectrometry Study (Recent Study)**
    - **Spectrum and Applications**
- **Future Study**

Working Principle



Positive: $P^n - me^- \leftrightarrow P^{n+m}$

Negative: $N^{n+m} + me^- \leftrightarrow N^n$

Electrical Energy ⇔ Chemical Energy ⇔ Storage

Vanadium Redox Flow System (VRFS)

- **VRFS has been studied for *25* years**
- **Positive V^{IV}/V^{V}: $VO^{2+} + 2H^{+} + e^{-} = VO^{++} + H_2O$**
- **Negative V^{II}/V^{III}: $V^{++} = V^{+++} + e^{-}$**
- ***3* M H_2SO_4**
- **Separated by proton-conducting membrane (*Nafion*)**
- **Carbon or Graphite Felt**

Advantageous:

- **Cross-contamination problems minimized**

Applications

More than 20 VRF battery systems have already been completed in Asia, Europe and the U.S.A..

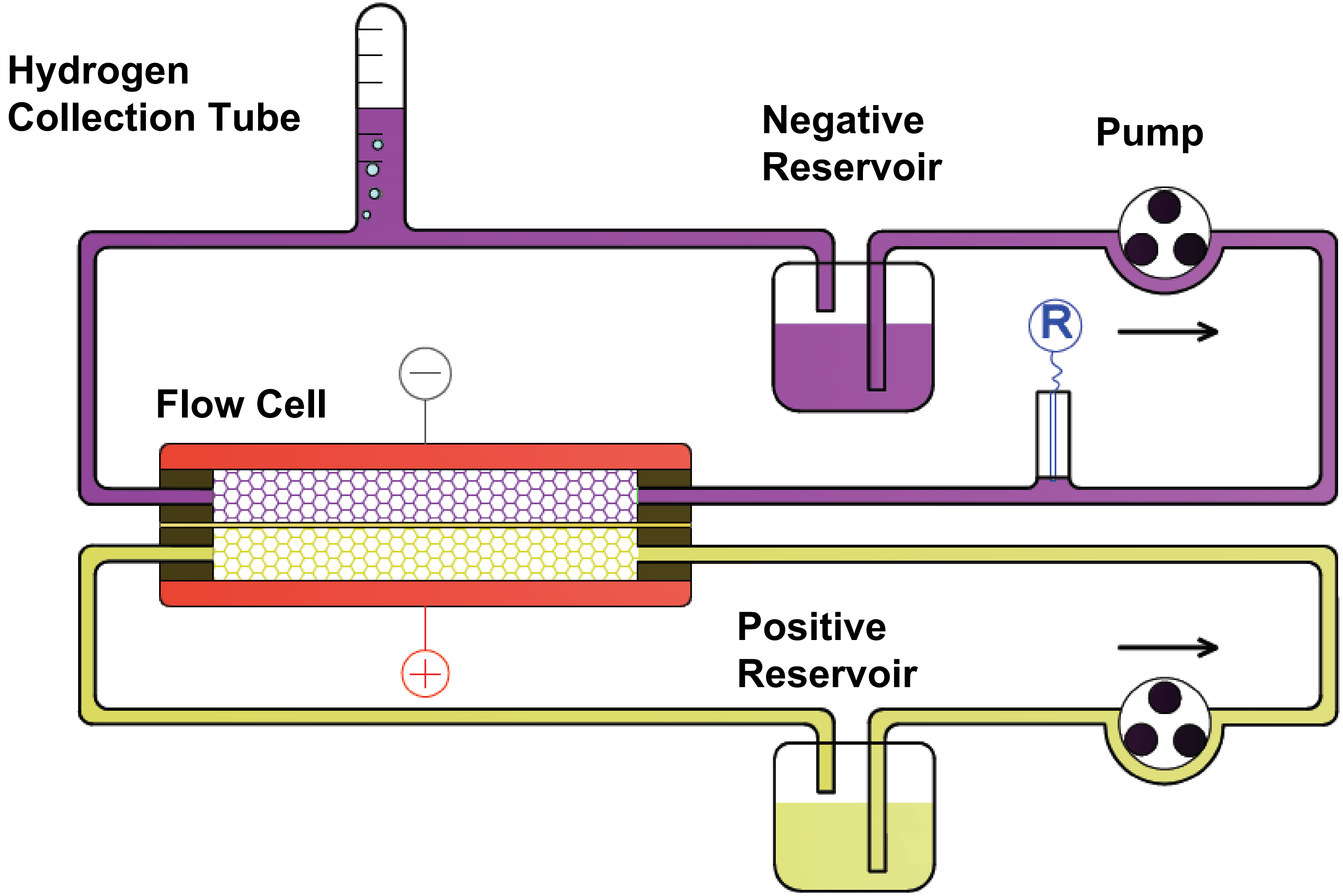
1. **200 kW/ 800 kWh installed by Mitsubishi Chemicals (1996) at Kashima-Kita Electric Power, Japan for load-levelling.**

2. **450 kW/ 900 kWh installed by Sumitomo Electric Industry (SEI) (1996) at Tasumi Sub-Station, Kansai Electric, Japan for peak shaving.**

3. **250 kW/500 kWh installed by VRB Power (2001) at Stellen-bosch University for ESKOM Power Corporation, South Africa for peak shaving and UPS back-up power.**

http://www.ceic.unsw.edu.au/centers/vrb/plist.htm

Experimental Setup

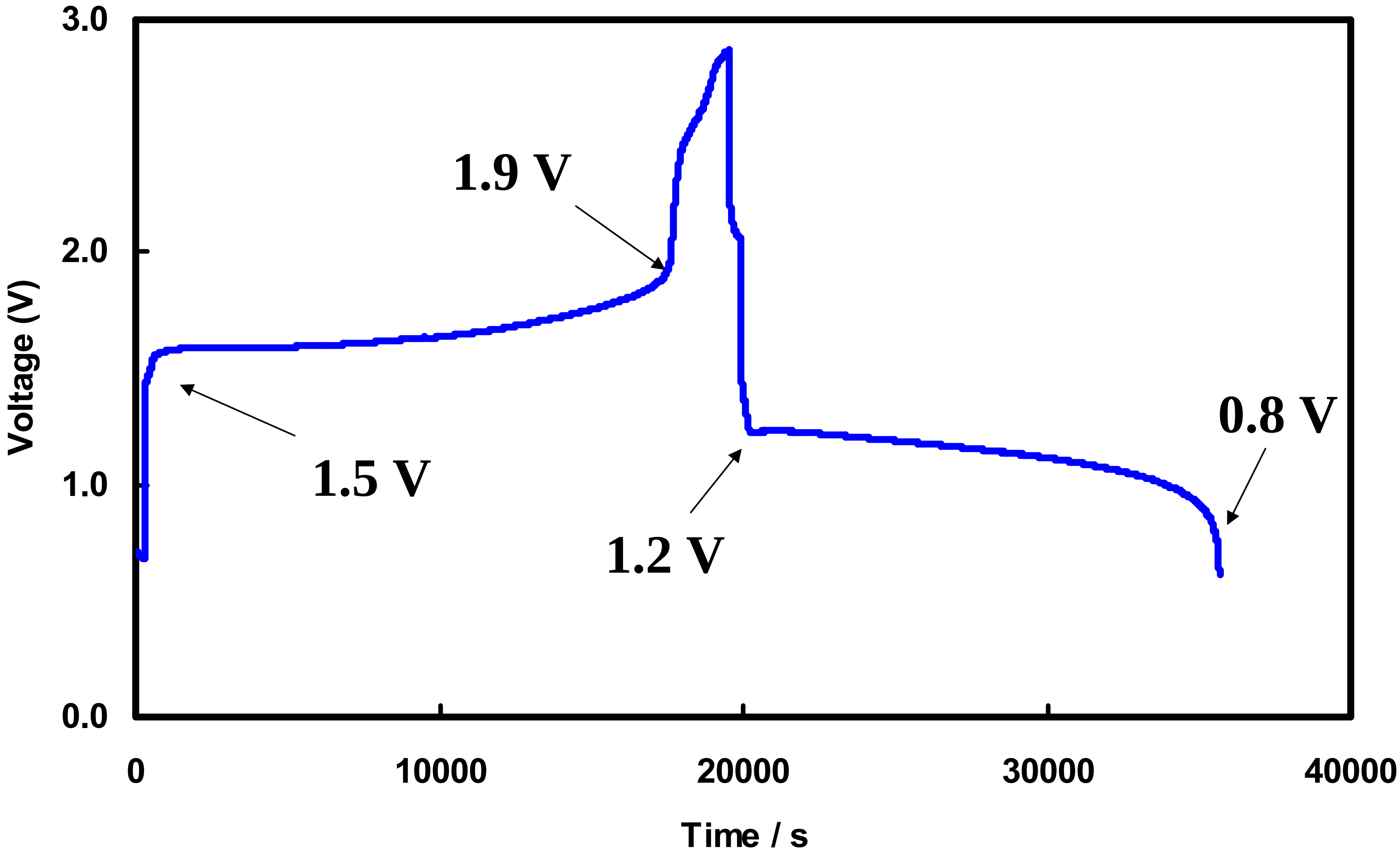


Experimental Conditions

- **Flow Cell**
  - Big Cell:16.24 cm^2
  - Small Cell: 5.25 cm^2
- **Flow Rate**
  - 0.44 $cm^3 s^{-1}$
  - 0.15 $cm^3 s^{-1}$
- **Temperature**
  - Reservoir: 25 ^0C
  - Room: 16 ~ 22 ^0C
- **Reference Electrode**
  - Hg/Hg_2SO_4 (SME)

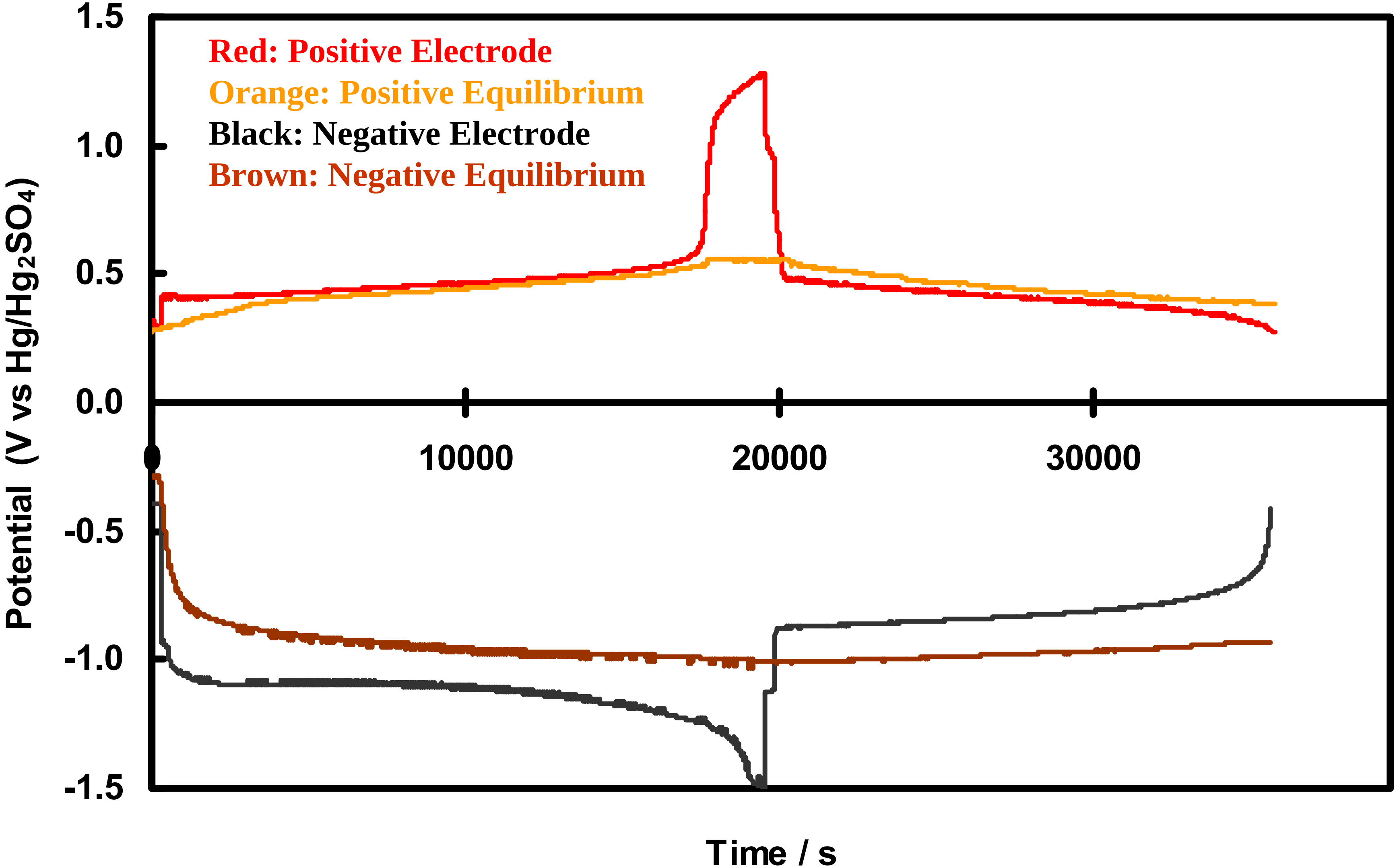
Charging and Discharging Battery

Full Charging and Discharging Curve, Battery Voltage, 40 mA cm^{-2}, 1.5 M Vanadium Solution in 3 M H_2SO_4

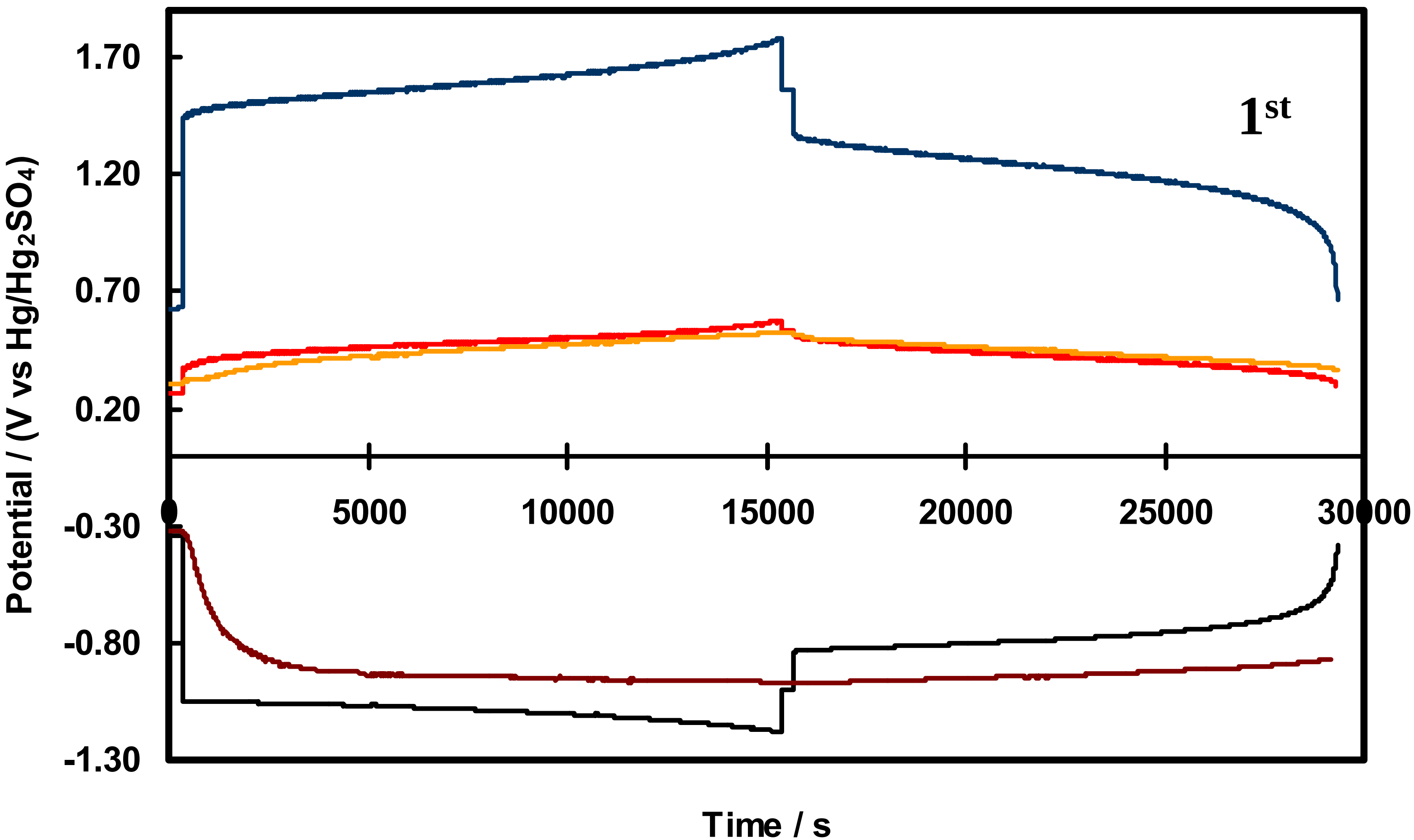


Columbic efficiency is around 90% whereas voltage efficiency is only 55%.

Full Charging and Discharging Curve, 40 mA cm^{-2}, Positive and Negative Electrodes, 1.5 M Vanadium Solution in 3 M H_2SO_4

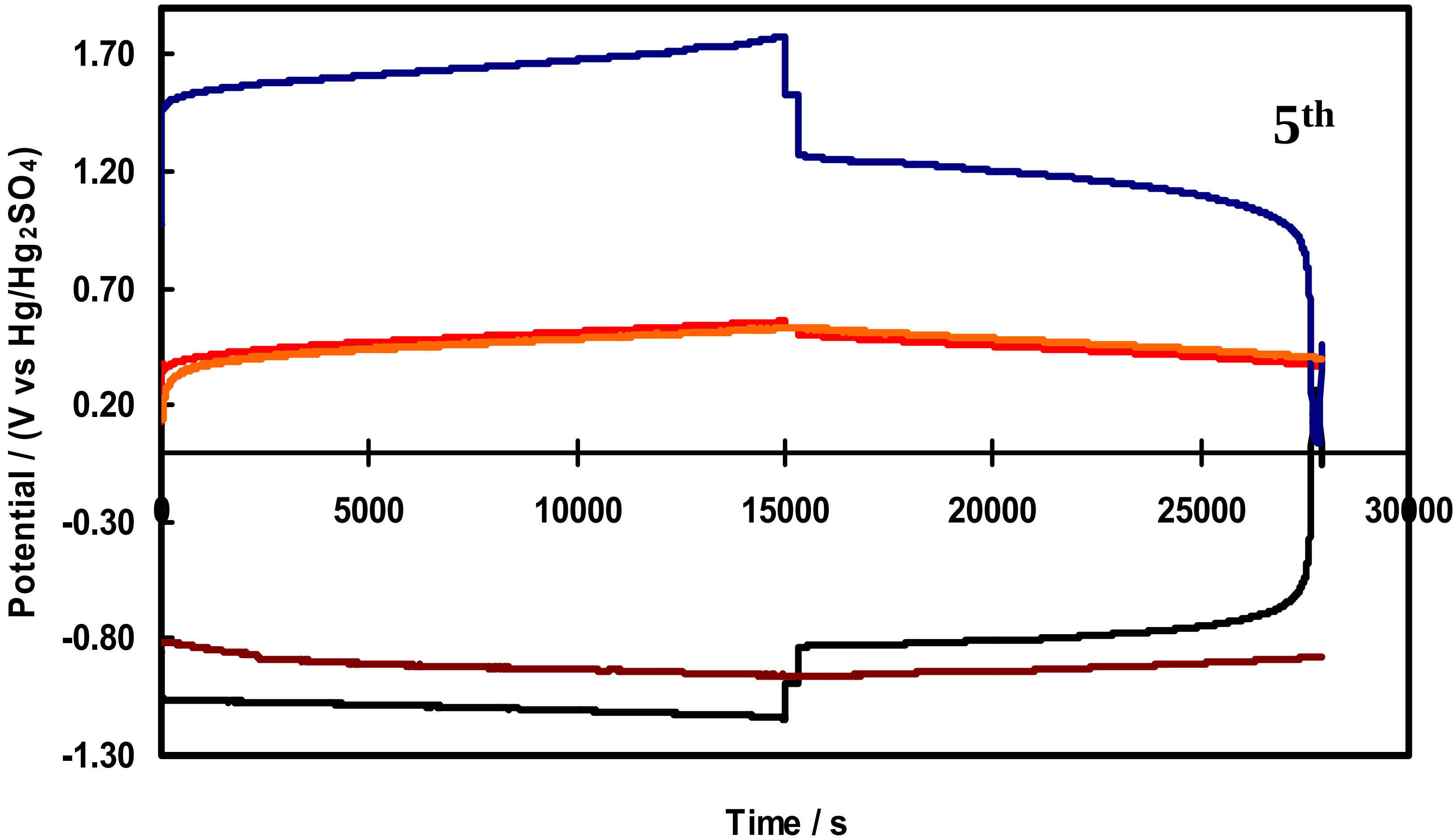


Charging and Discharging Curves, 40 mA cm^{-2}, 1.5 M Vanadium Solution in 3 M H_2SO_4



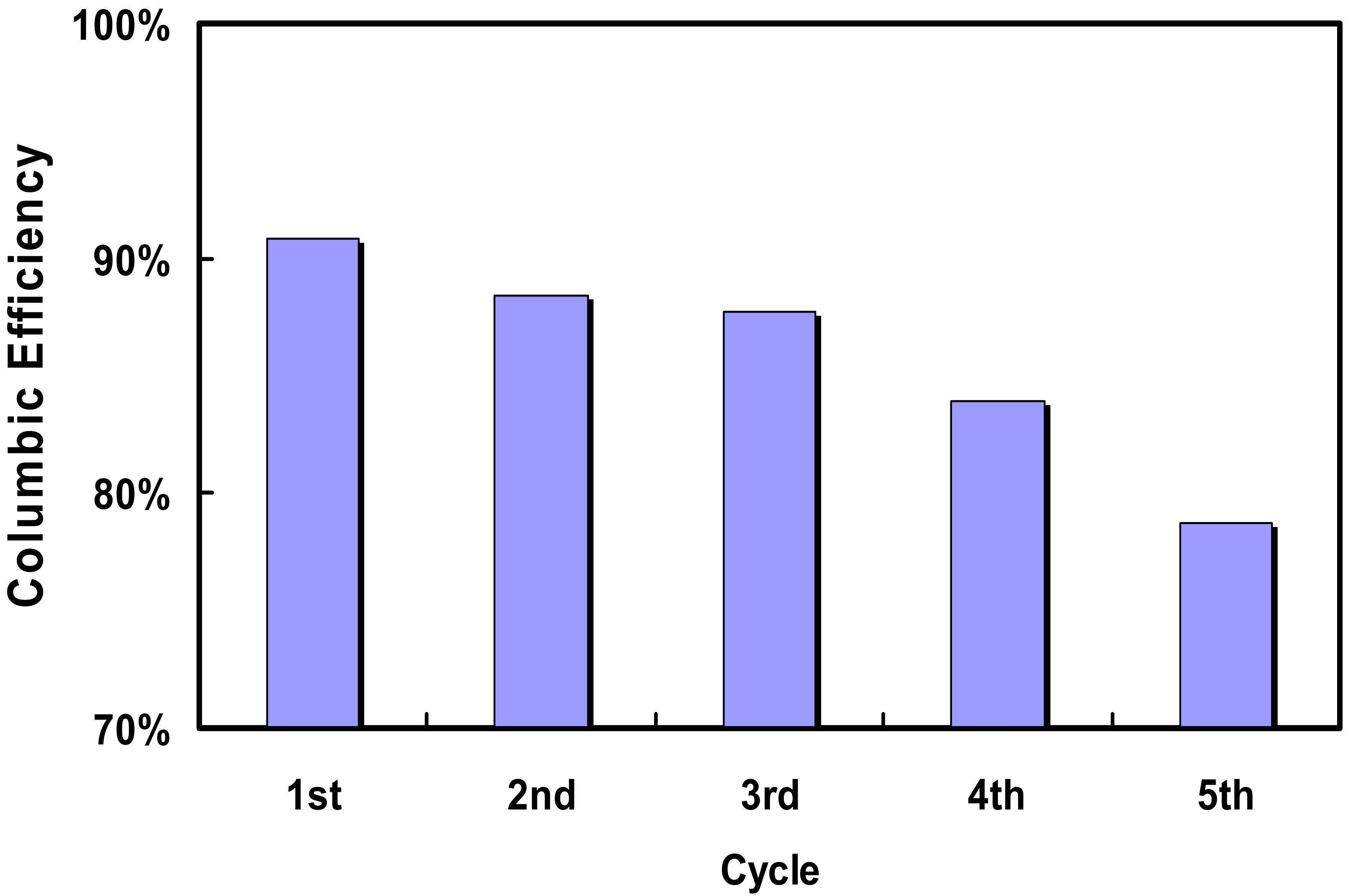
Columbic efficiency is around 92%

Charging and Discharging Curves, 40 mA cm^{-2}, 1.5 M Vanadium Solution in 3 M H_2SO_4



Columbic efficiency is around 78%

Columbic Efficiency



Conclusions

- Negative overpotential is bigger than positive overpotential.
- Battery's life is limited by the negative electrode.
- **Hydrogen is formed at the negative electrode.**

* Hydrogen Evolution during Preparation of Anolyte

*This result has been first presented by Prof. D. N. Buckley on ECS Meeting 2010,Vancouver, BC, Canada.

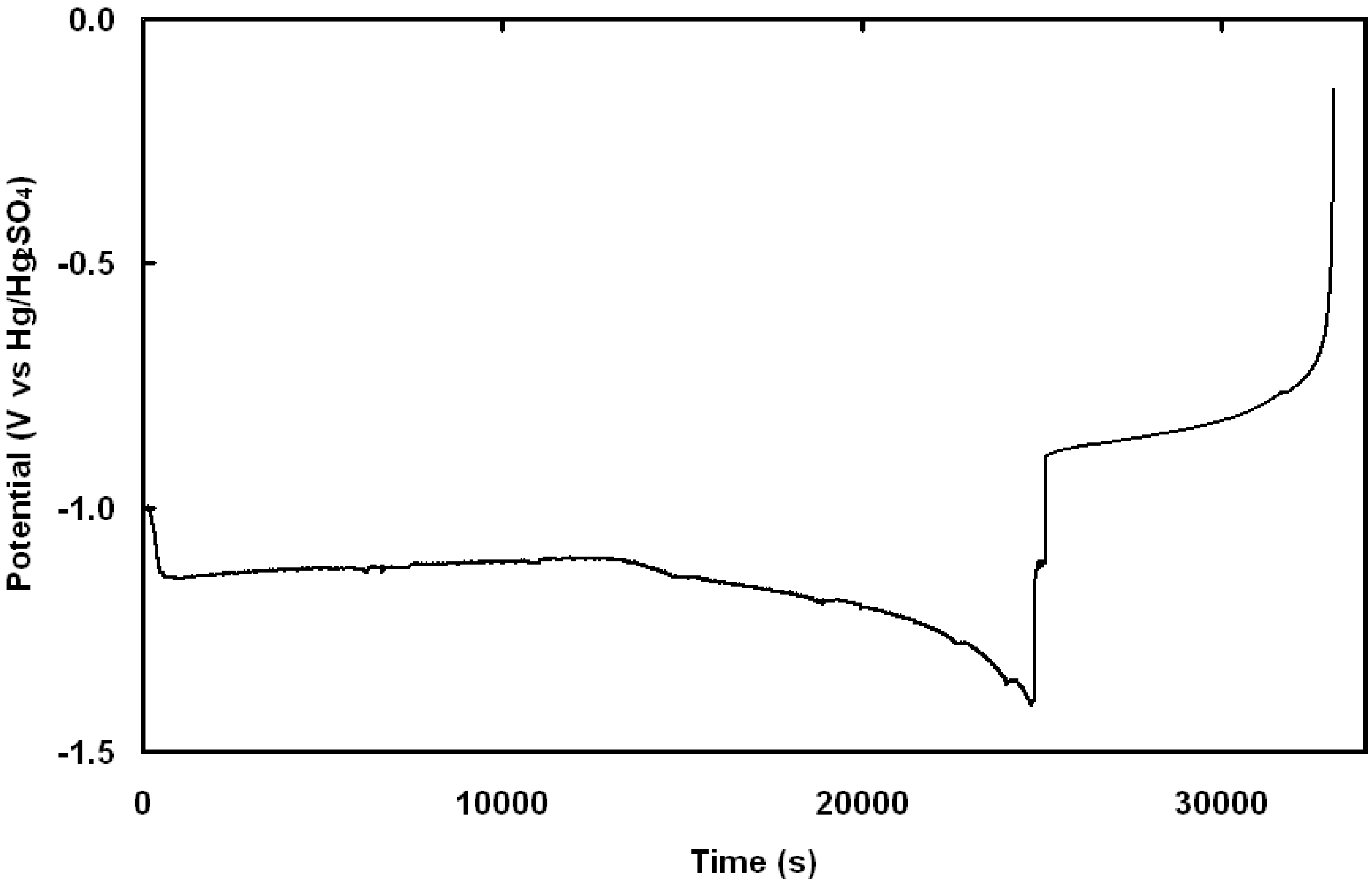
Reduction of VO^{++} and V^{+++}

- $VO^{++} + 2H^{+} + e^{-} = V^{+++} + H_2O$
  - E_0 = 0.337 V (SHE)
  - = –0.303 V (SME)
  - High overpotential

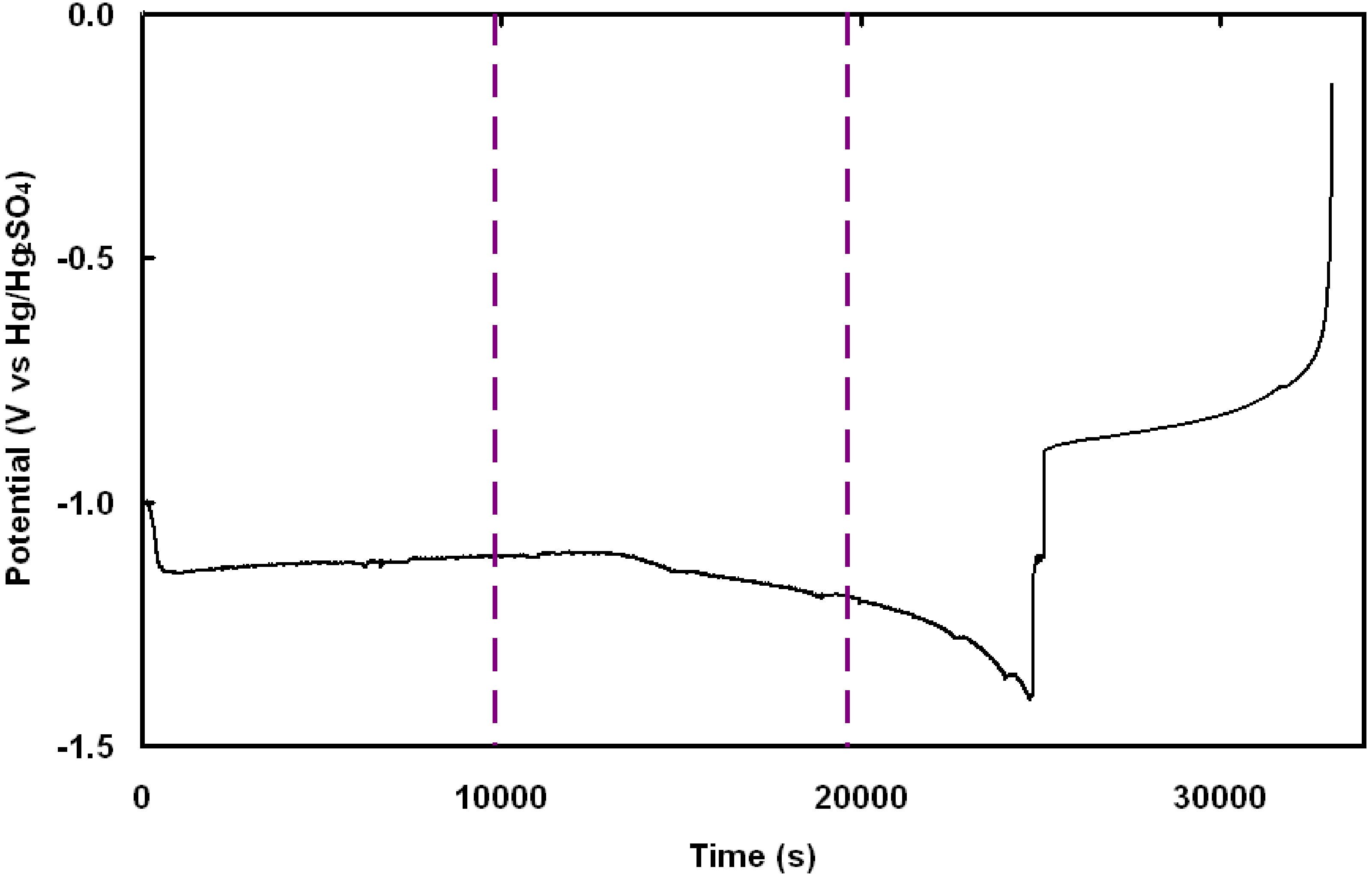
- $V^{+++} + e^{-} = V^{++}$
  - E_0 = –0.291 V (SHE)
  - = –0.931 V (SME)

- Thermodynamically expect hydrogen

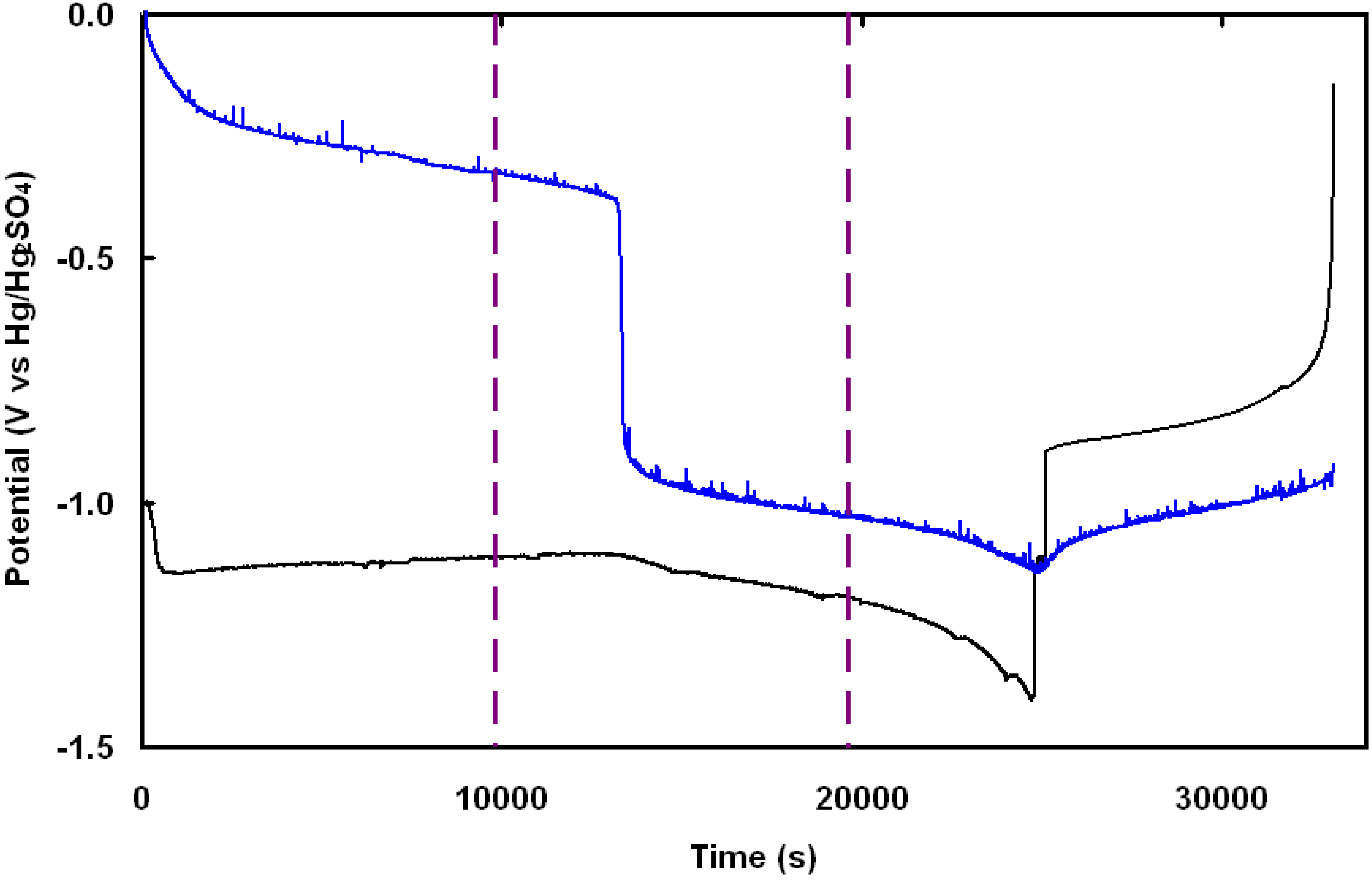
Charging Curve, Negative Electrode, 40 mA cm^{-2}, 1.5 M $VOSO_4$ in 3 M H_2SO_4



Charging Curve, Negative Electrode, 40 mA cm^{-2}, 1.5 M $VOSO_4$ in 3 M H_2SO_4

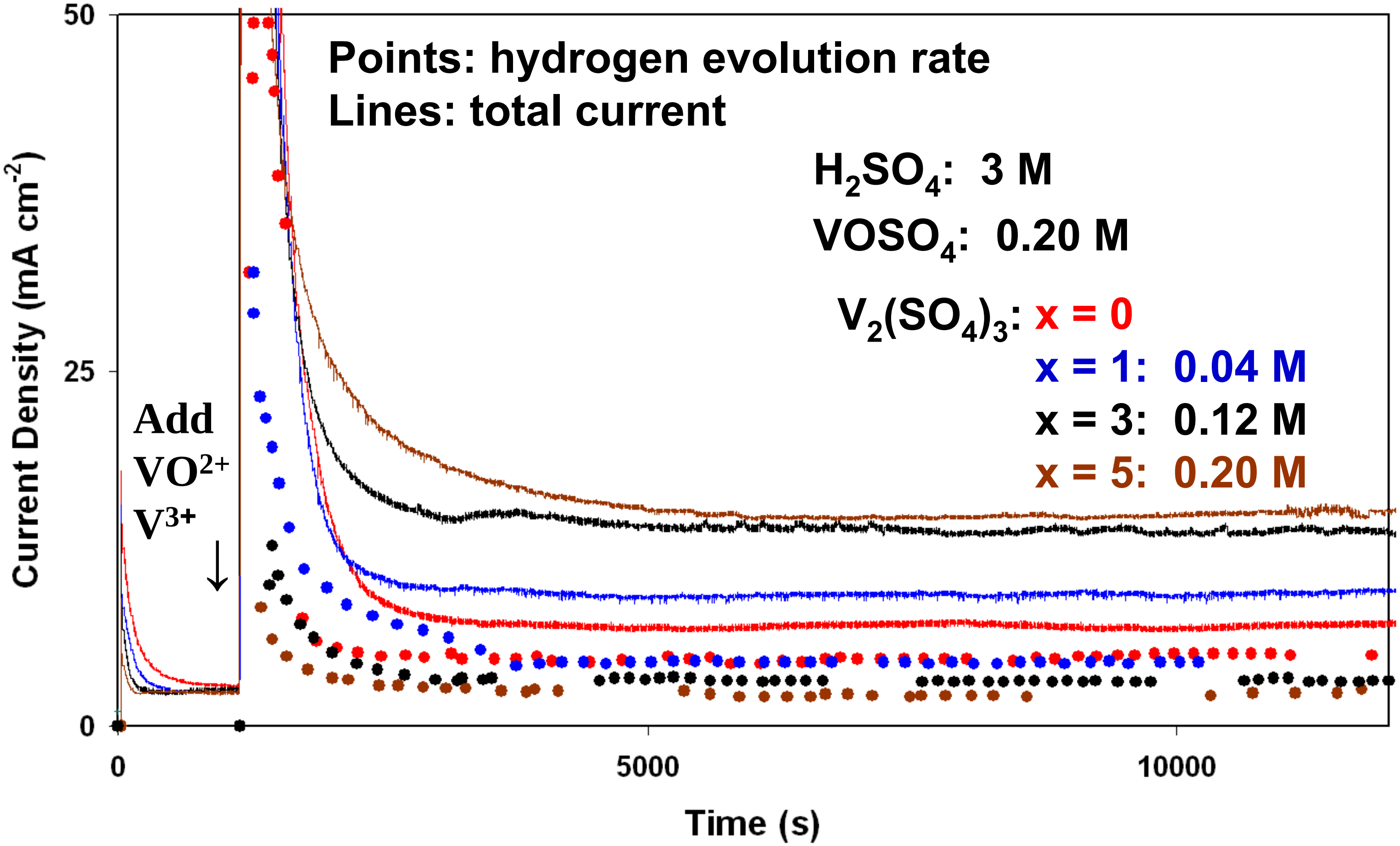


Charging Curve, Negative Electrode, 40 mA cm^{-2}, 1.5 M $VOSO_4$ in 3 M H_2SO_4

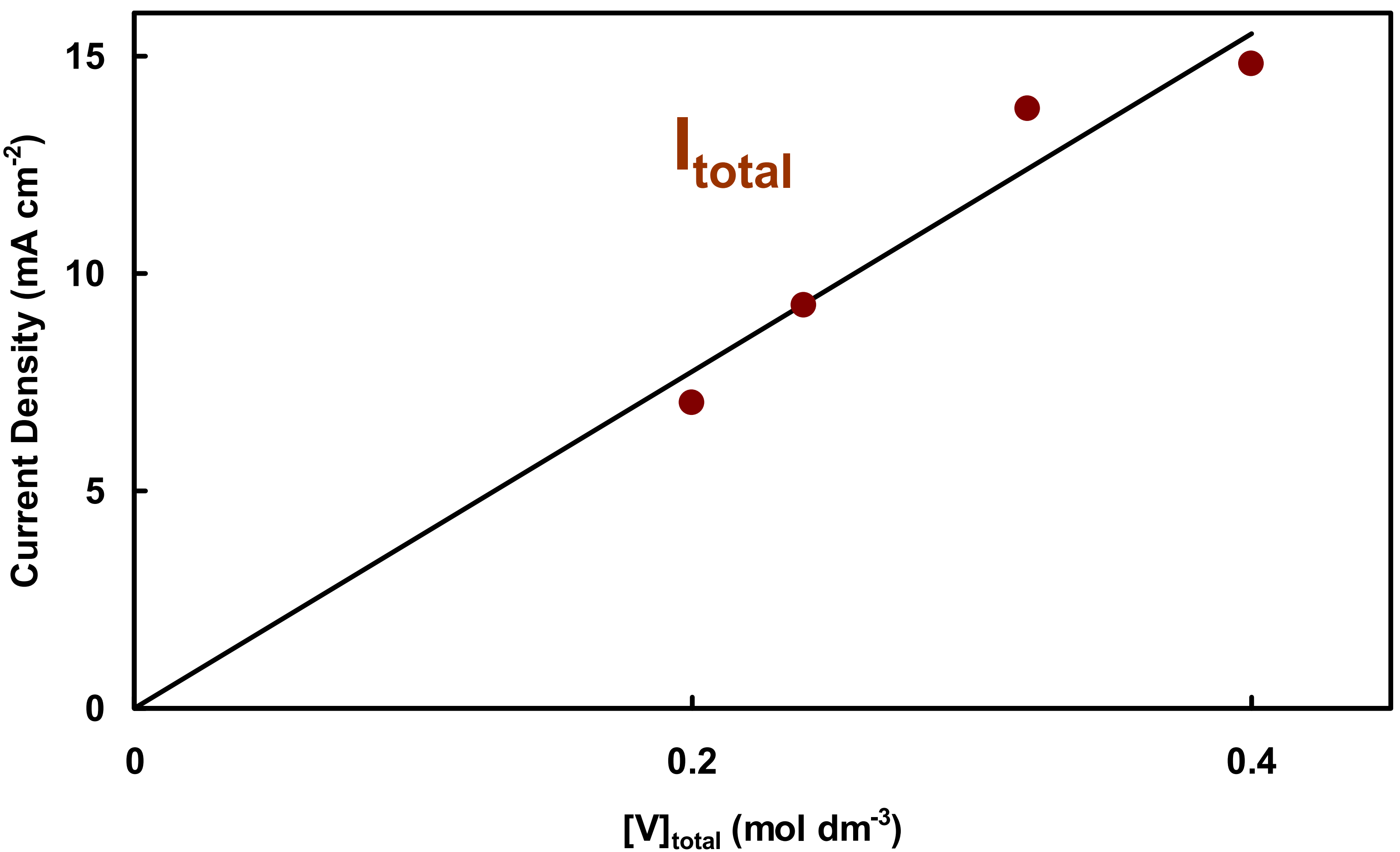


Addition of VO^{2+}/V^{3+} to 3 M H_2SO_4

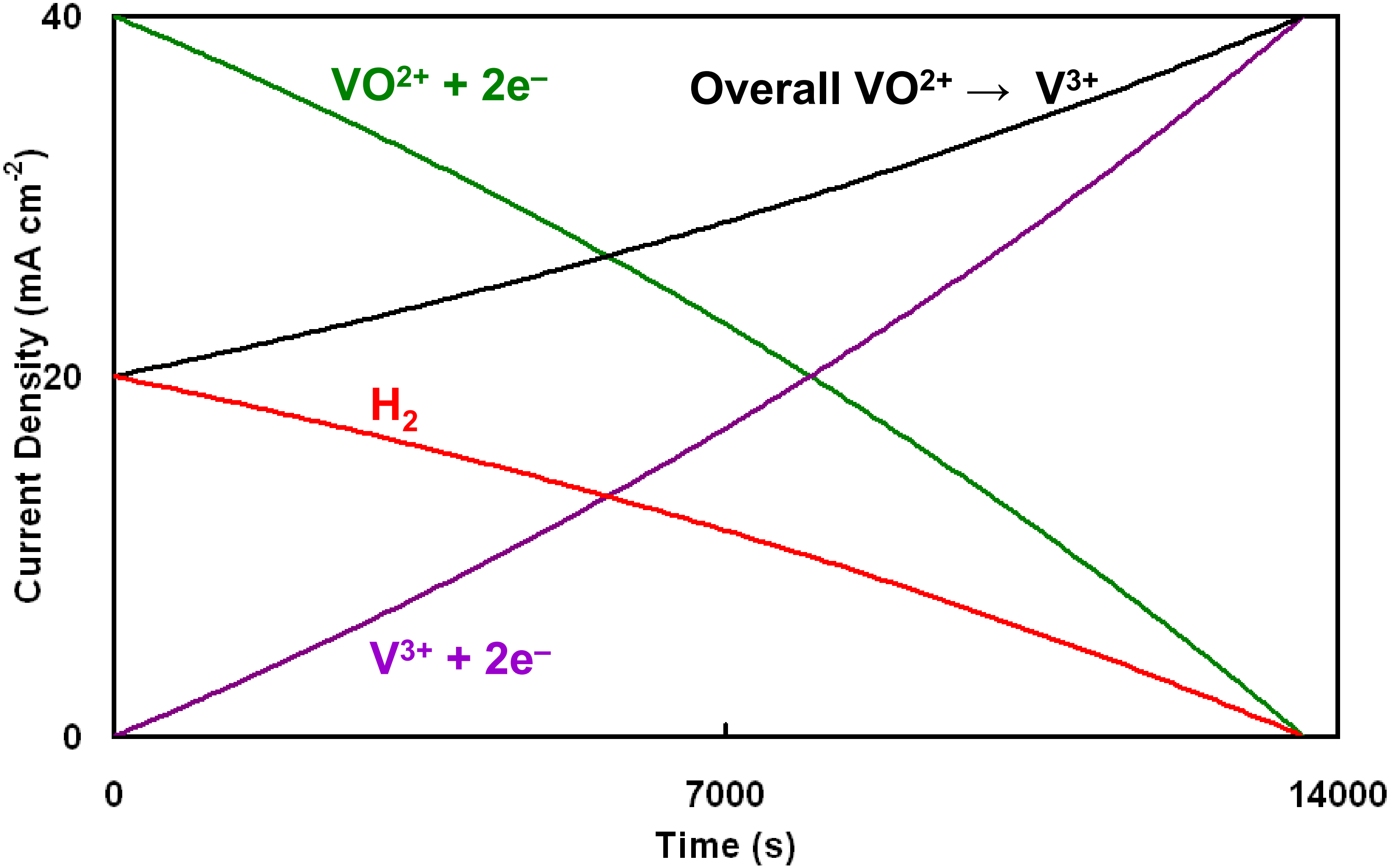
Potential: –1.05 V (Hg/Hg_2SO_4)
Add 12.5 mL to 25 mL 3 M H_2SO_4
(5 mL 1.5 M $VOSO_4$ + x mL 1.5 M $V_2(SO_4)_3$;
balance to 12.5 mL; $[H_2SO_4]$ = 3 M)



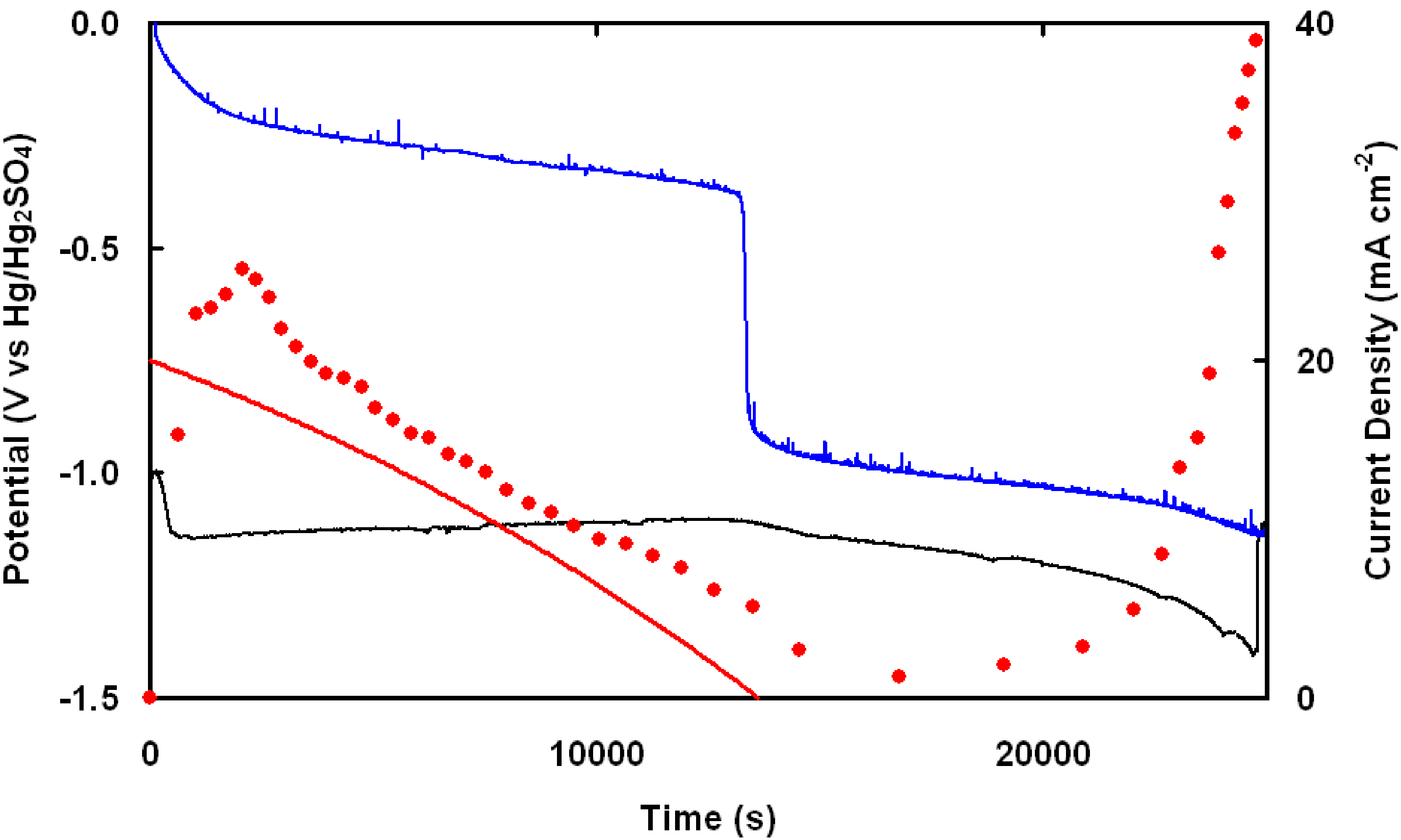
Addition of VO^{2+}/V^{3+} to 3 M H_2SO_4



Model Predictions: VO^{2+} Reduction and Hydrogen Evolution



Comparison with Experiment



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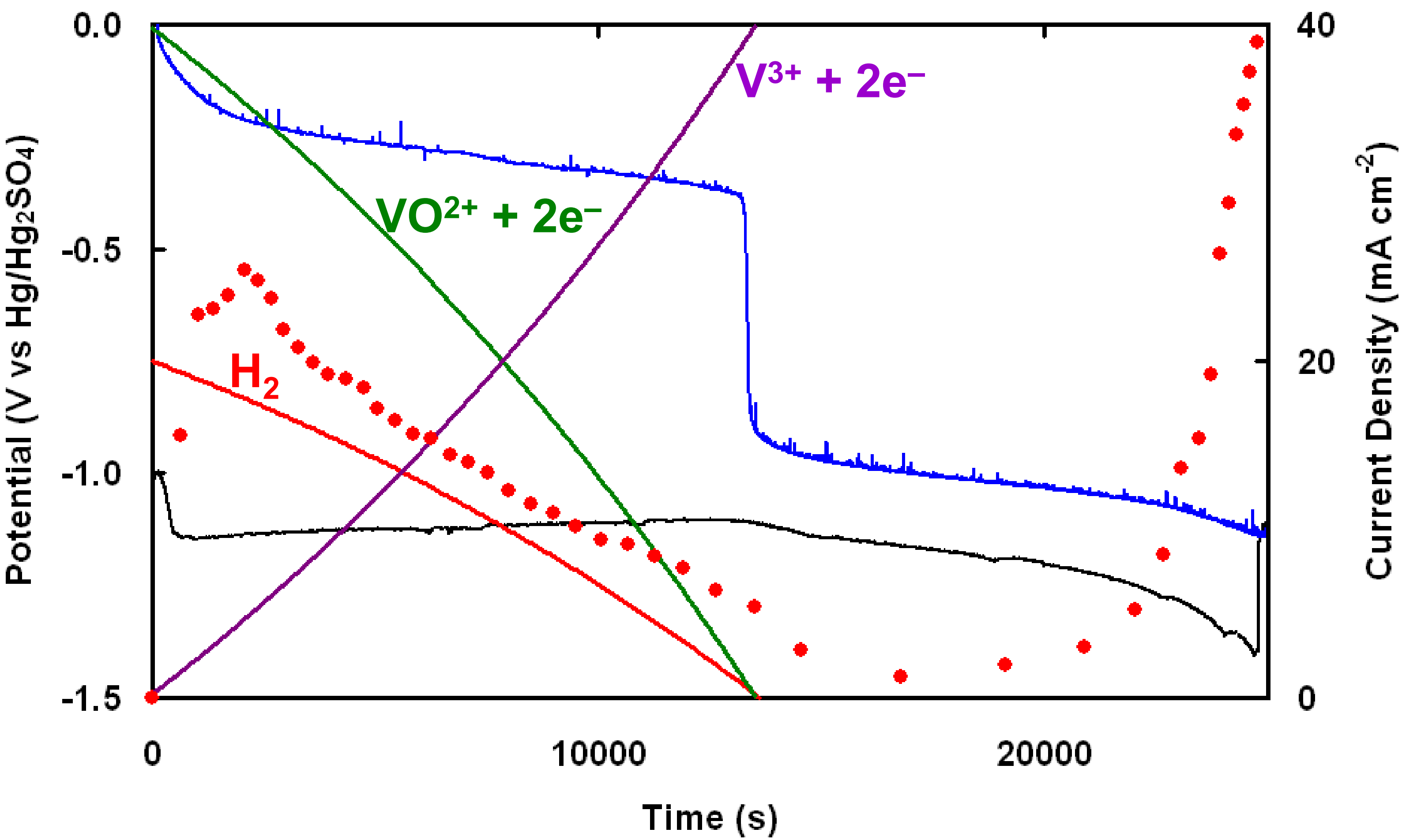


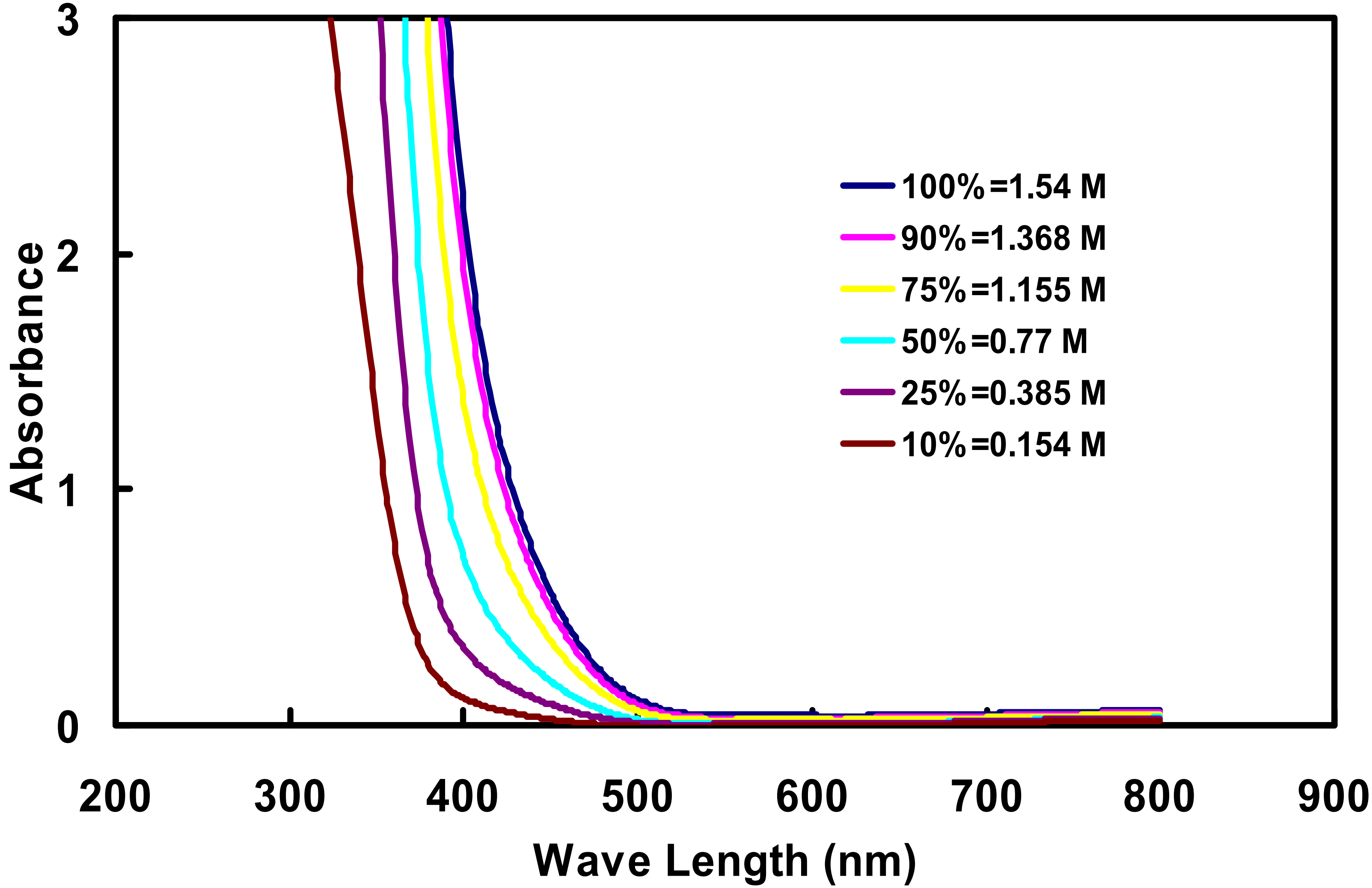
Conclusions

- Presence of VO^{++} enhances hydrogen evolution on carbon felt in 3 M H_2SO_4
- Formation of a reactive intermediate V^{II}
- Simple model gives reasonable agreement with results

Spectrometry Study

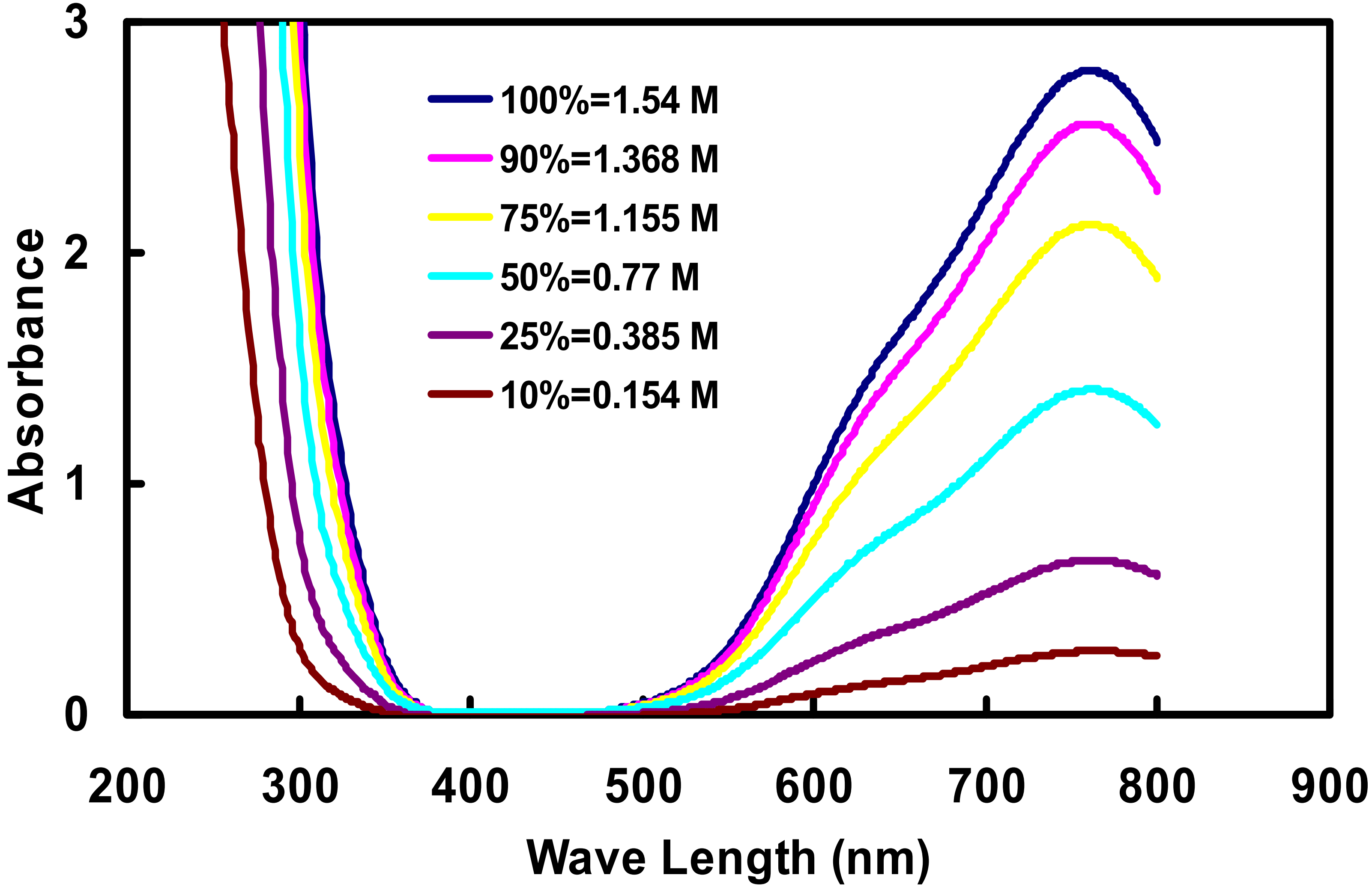
- **The colour of Vanadium ions in H_2SO_4 show:**
  - **V^{V}: Yellow**
  - **V^{IV}: Blue**
  - **V^{III}: Green**
  - **V^{II}: Purple**

V^V Spectrum

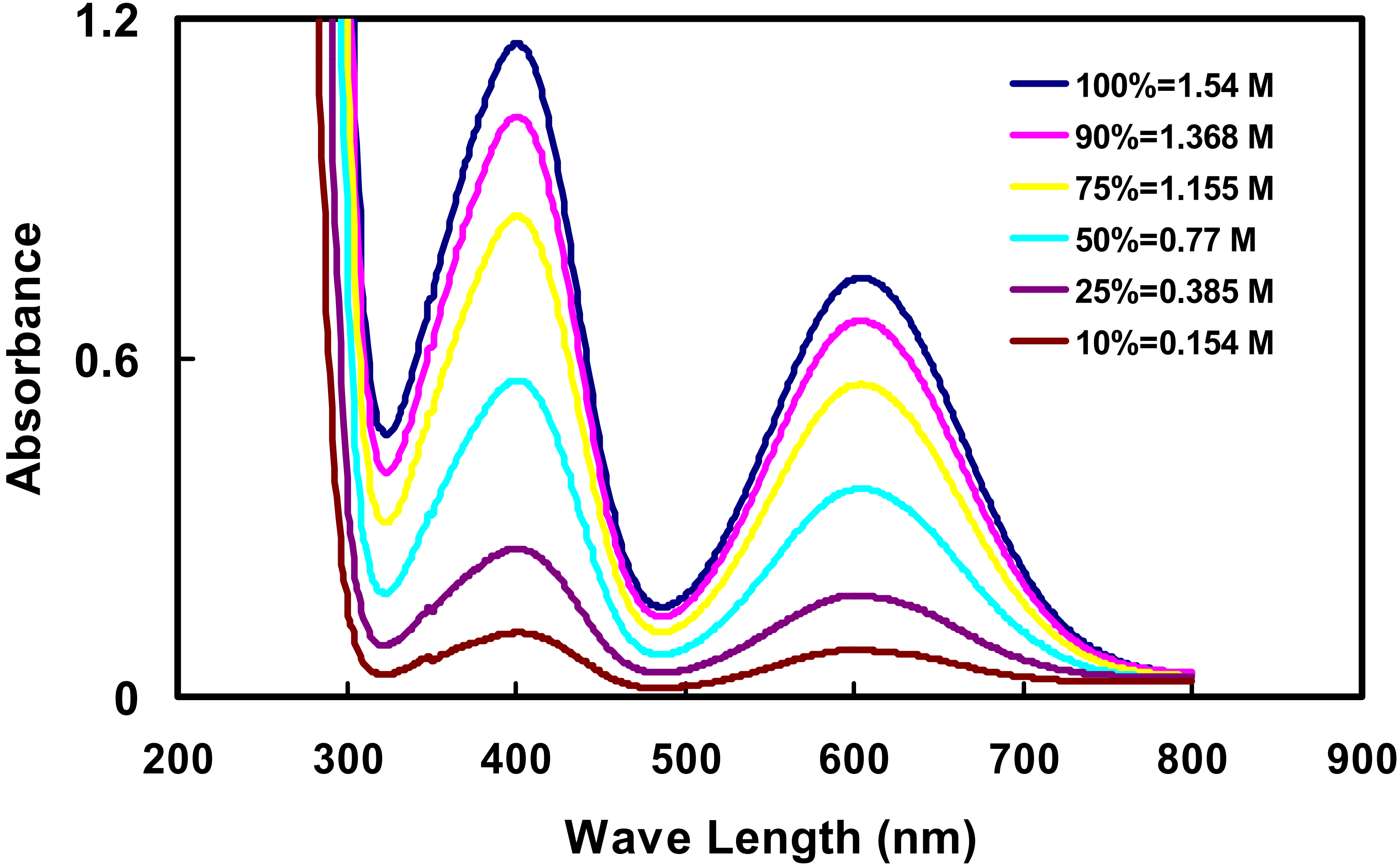


3
2
1
0
Absorbance
200
300
400
500
600
700
800
900
Wave Length (nm)
100%=1.54 M
90%=1.368 M
75%=1.155 M
50%=0.77 M
25%=0.385 M
10%=0.154 M

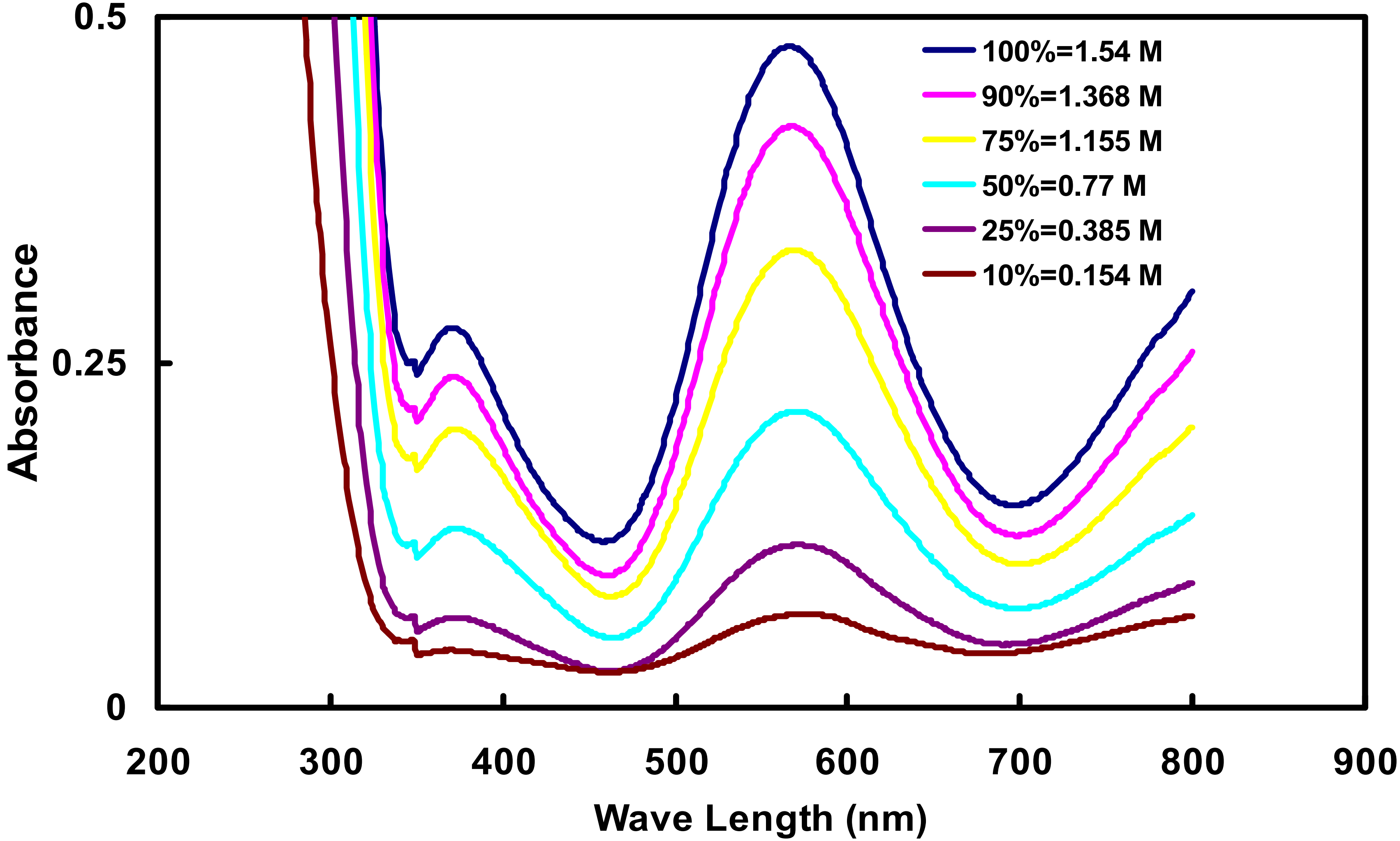
V^{IV} Spectrum



V^{III} Spectrum



V^{II} Spectrum



Future Work

- **State of Charge**
- **Chemical titration**
- **Cyclic Voltammetry**
- **Chemical treatment of carbon felt**
- **Battery design**

Acknowledgements

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