

# Inter-compartment concentration monitoring of key species in a vanadium redox flow battery operating with and without polarization: experiments and construction of a predictive model

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# Introduction / objectives

## Vanadium Redox Flow Battery (VRFB)

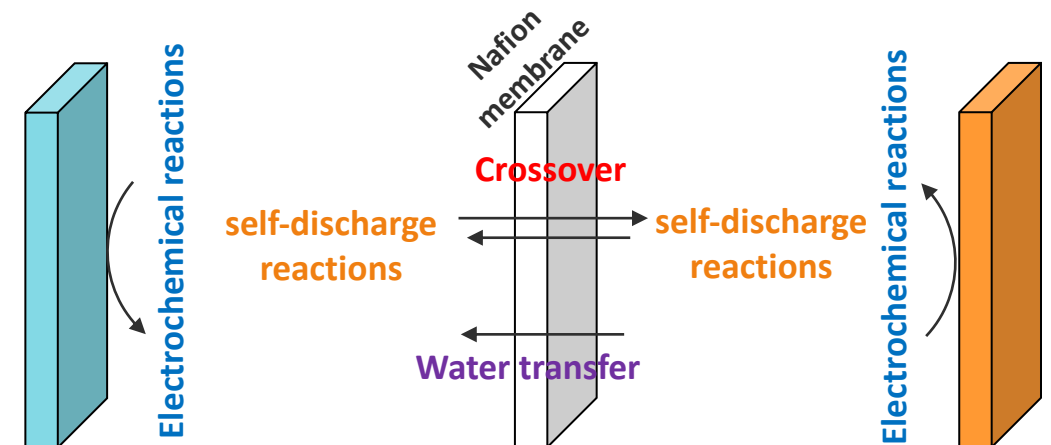
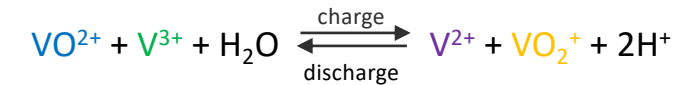
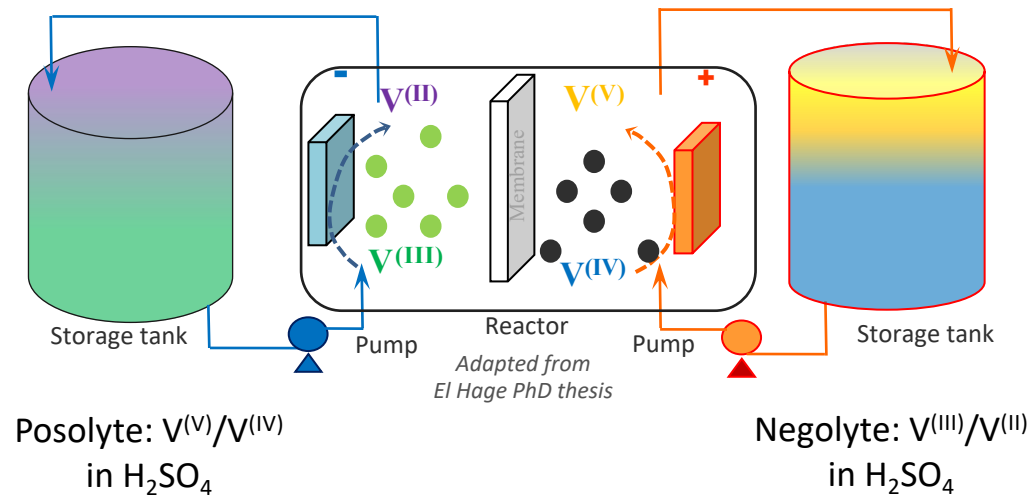
- Aqueous RFB,  $\Delta V = 1.26$  V, recyclable (no chemical degradation) 👍
- The same element on both sides → no poisoning 👍
- Small size of Vanadium ions  
→ **crossover difficult to avoid** and **self-discharge reactions** 👎
- **Water transfer**
- Variation of the acidity

### ► Complex temporal evolution of the composition (Vanadium species, acid, water)

- Decrease of the storage capacity
- Precipitation issues (solubility of V ions = f(pH, T))
- Battery lifespan limited  
→ management of the storage tanks (pH & water adjustments, regeneration by mixing)

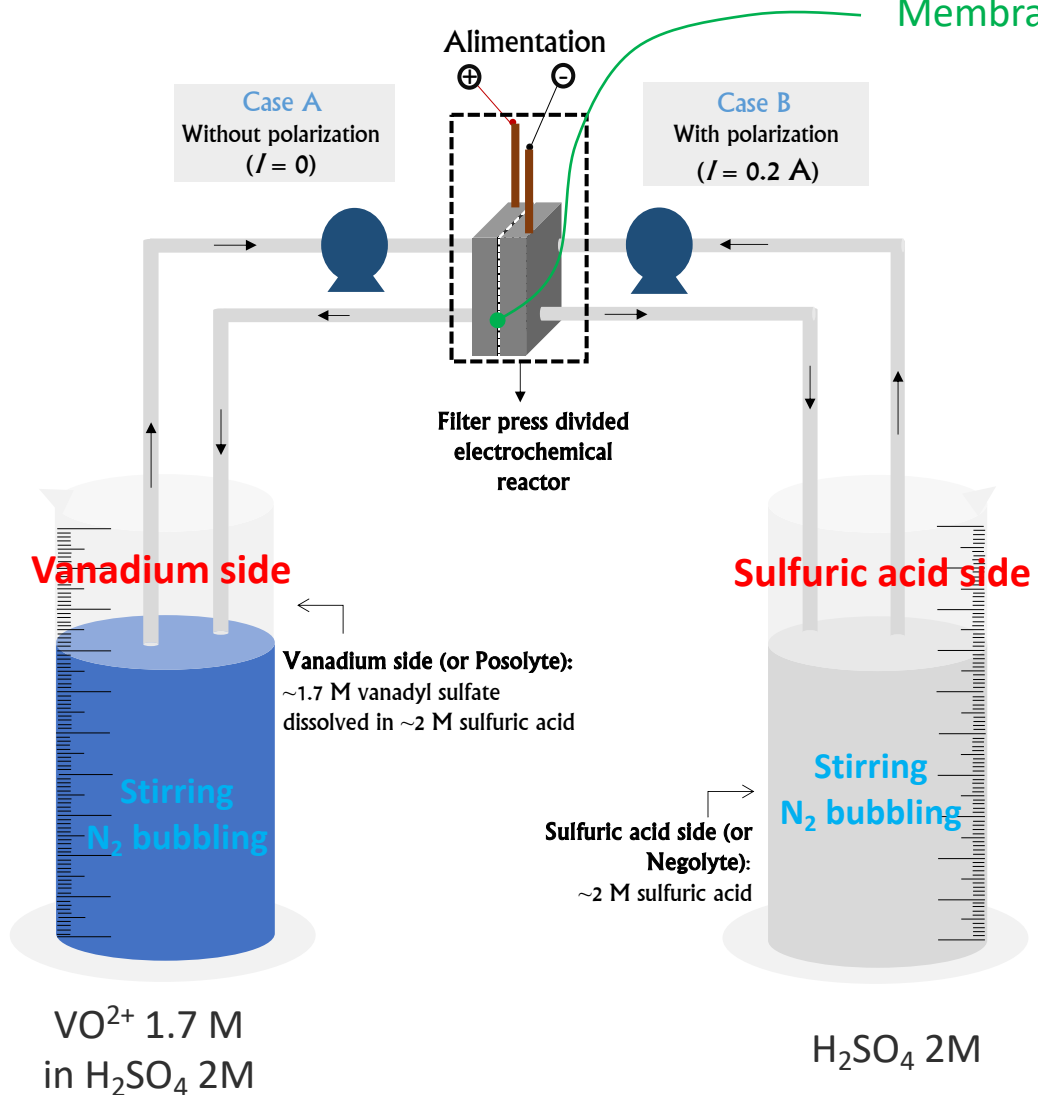
→ Experimental measurements with a lab-scale VRFB

→ Modelling of vanadium, water and acid inter-compartment transfers

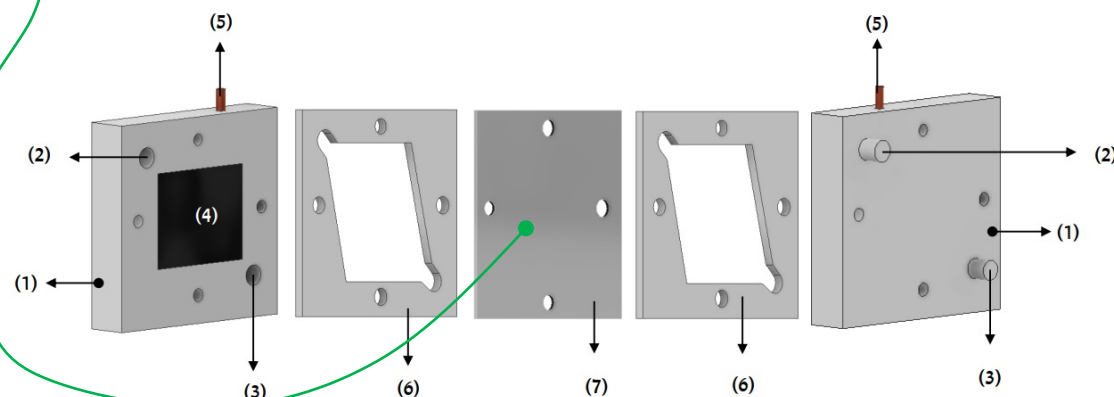


# Experiments

Membrane : Nafion 424

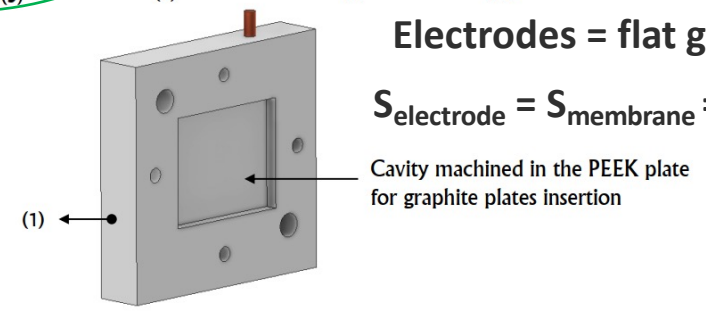


## Filter-press electrochemical reactor



Electrodes = flat graphite

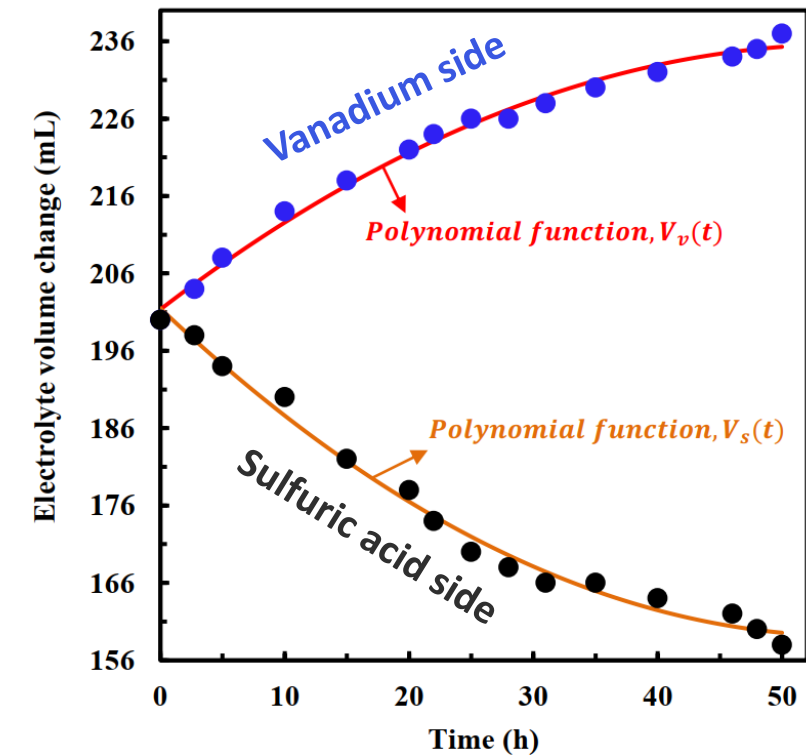
$$S_{\text{electrode}} = S_{\text{membrane}} = 20 \text{ cm}^2$$



## Analytical techniques

- UV-vis:  $V^{2+}$ ,  $V^{3+}$  and  $VO^{2+}$
- Potentiometric titrations:  $VO_2^+$  and acid
- Storage tank level: water volume

# Experiment Result: case A, $I = 0$

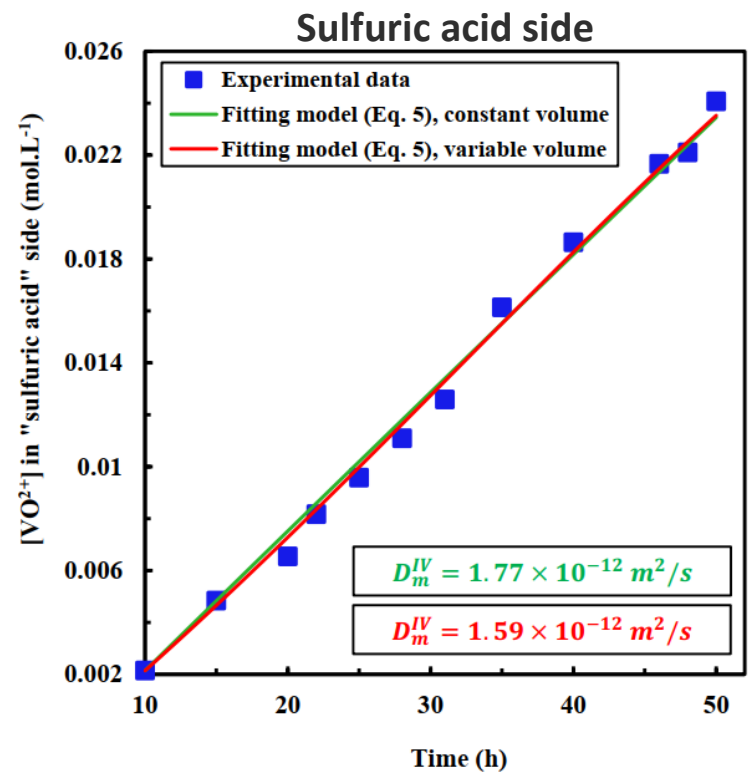
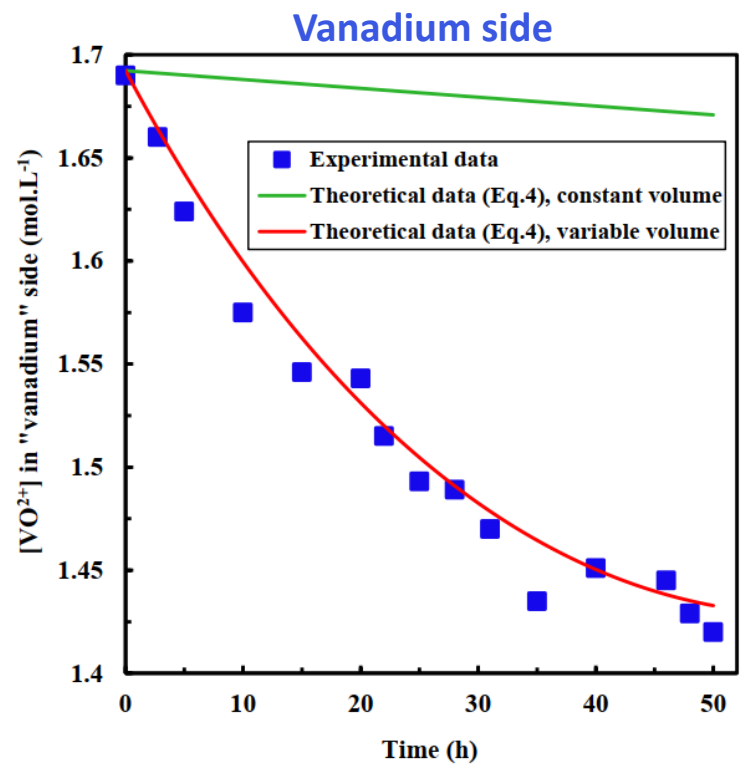


Initial osmotic pressure  
~40 bar (van't Hoof law)

Mass balance

Diffusion flux (Fick's law)

Coupled ODEs solved  
(python)



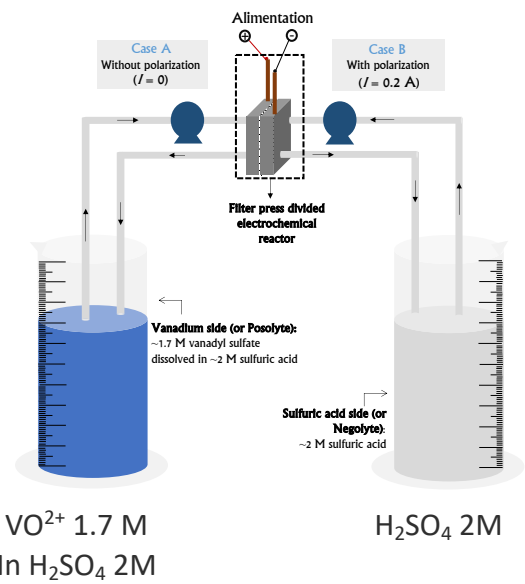
$$\frac{d(c_v^{IV} \cdot V_v)}{dt} = -J_{diff}^{IV}$$

$$\frac{d(c_s^{IV} \cdot V_s)}{dt} = +J_{diff}^{IV}$$

$$J_{diff}^{IV} = -S_m \cdot D_m^{IV} \cdot \frac{(c_s^{IV} - c_v^{IV})}{L}$$

$$\frac{dc_v^{IV}}{dt} = \frac{1}{V_v} \left[ -J_{diff}^{IV} - c_v^{IV} \frac{dV_v}{dt} \right], \quad c_v^{IV}(0) = 1.7 \text{ M} \quad \frac{dc_s^{IV}}{dt} = \frac{1}{V_s} \left[ J_{diff}^{IV} - c_s^{IV} \frac{dV_s}{dt} \right], \quad c_s^{IV}(0) = 0$$

# Experiment Result: case A, $I = 0$



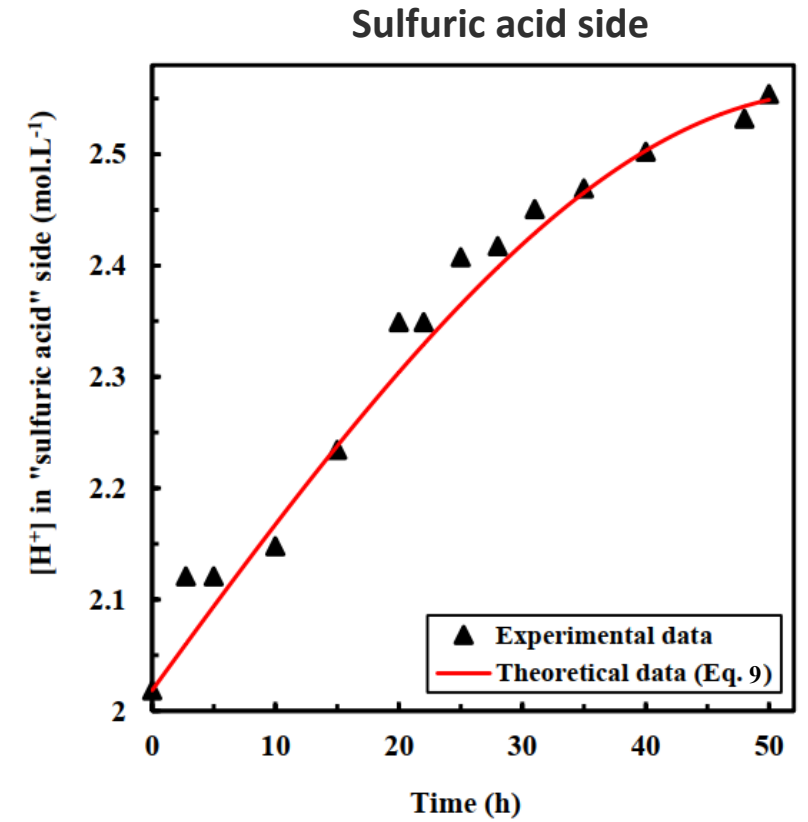
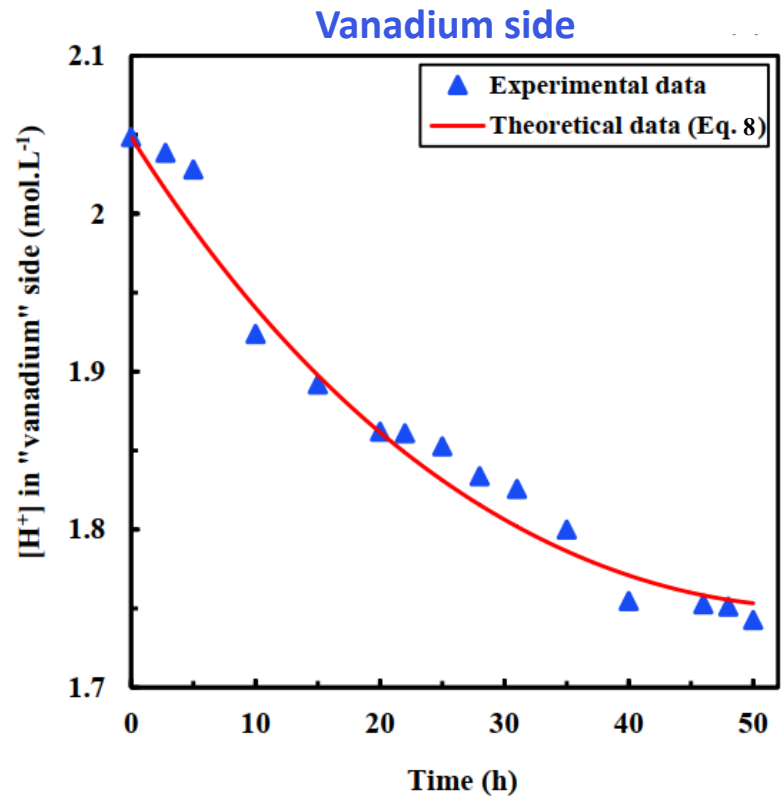
Vanadium side

Sulfuric acid side

Mass balance

Diffusion flux (Fick's law)

Coupled ODEs solved



$$\frac{d(c_v^{H^+} \cdot V_v)}{dt} = -J_{diff}^{H^+}$$

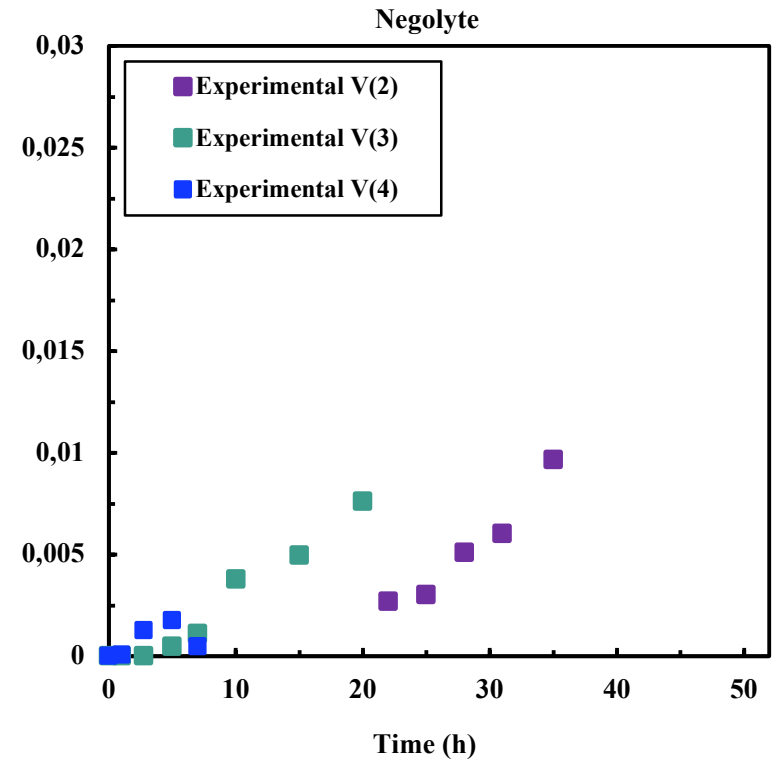
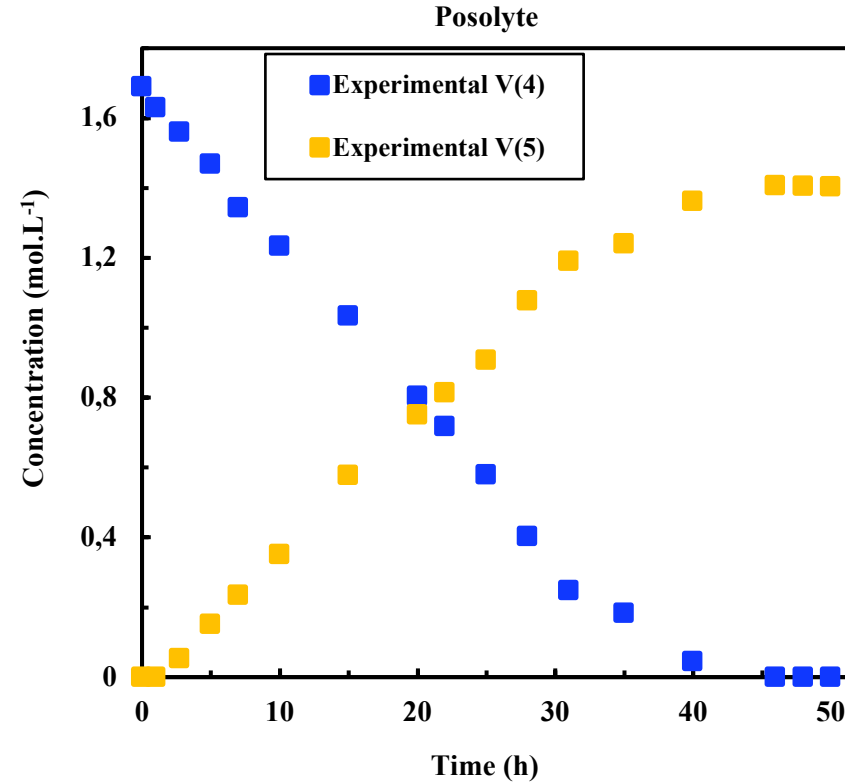
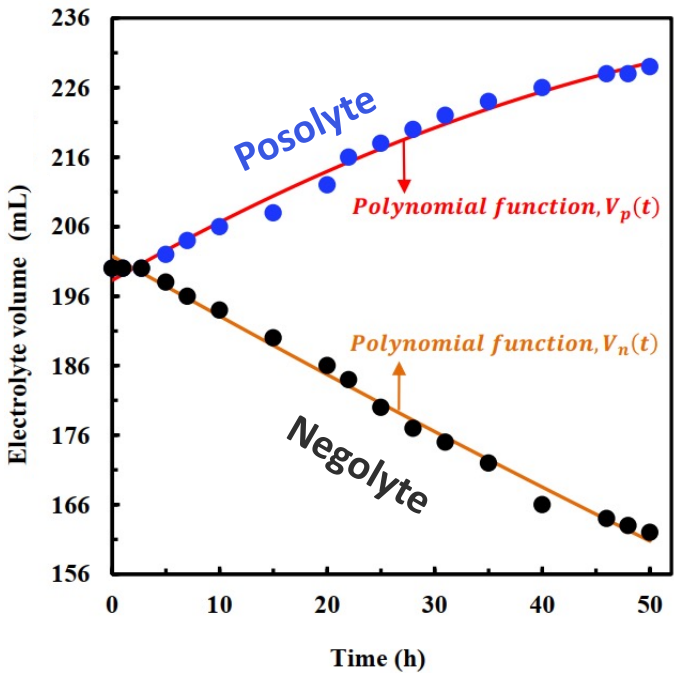
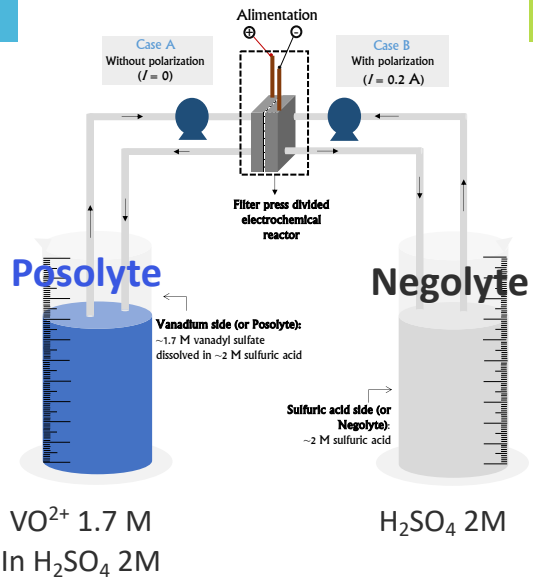
$$\frac{d(c_s^{H^+} \cdot V_s)}{dt} = +J_{diff}^{H^+}$$

$$J_{diff}^{H^+} = -S_m \cdot D_m^{H^+} \cdot \frac{(c_s^{H^+} - c_v^{H^+})}{L} \approx 0$$

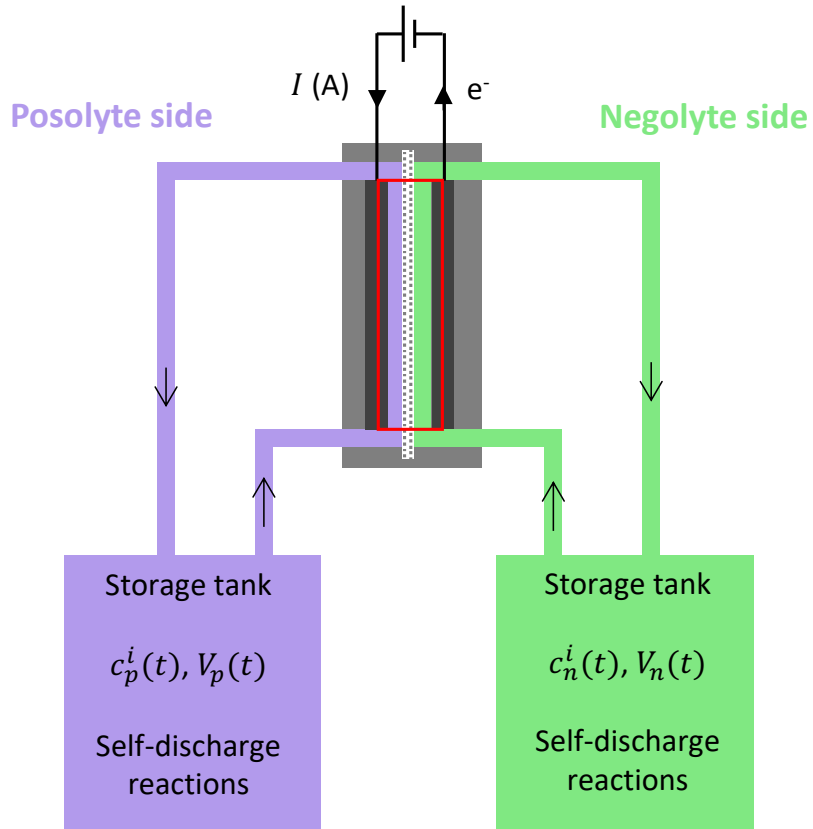
$$\frac{dc_v^{H^+}}{dt} = \frac{1}{V_v} \left[ 0 - c_v^{H^+} \frac{dV_v}{dt} \right]$$

$$\frac{dc_s^{H^+}}{dt} = \frac{1}{V_s} \left[ 0 - c_s^{H^+} \frac{dV_s}{dt} \right]$$

# Experiment Result: case B, $I = 0.2 \text{ A}$ ( $10 \text{ mA/cm}^2$ )



# Modeling



## Considerations and assumptions

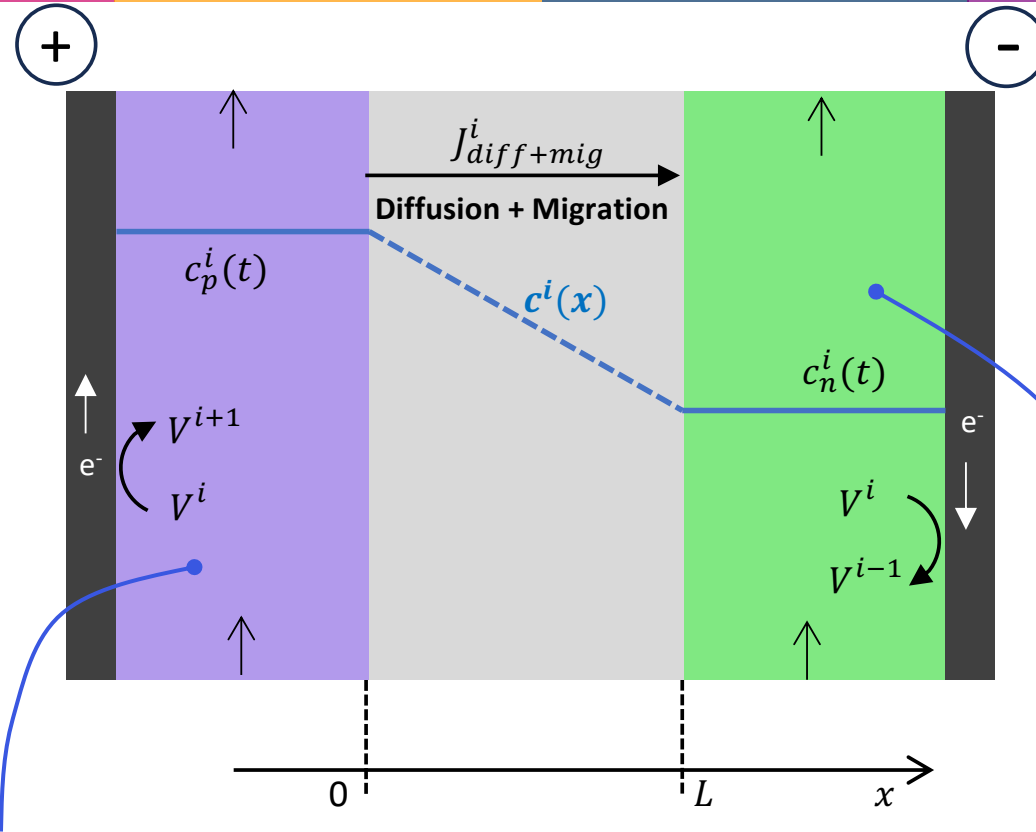
Uniform concentration, dilute solution approximation

Volume variations

Transport by diffusion and migration

Electrochemical reactions

Self-discharge reactions



$$\frac{dc_p^i}{dt} = \frac{1}{V_p} \left[ -J_{diff+mig}^i + J_{p,elec}^i + \alpha^i - c_p^i \frac{dV_p}{dt} \right]$$

$$i : V^{2+}, V^{3+}, VO^{2+}, VO_2^+$$

$$\frac{dc_p^{H^+}}{dt} = \frac{1}{V_p} \left[ -J_{mig}^{H^+} + J_{p,elec}^{H^+} - c_p^{H^+} \frac{dV_p}{dt} \right]$$

$$\frac{dc_n^i}{dt} = \frac{1}{V_n} \left[ +J_{diff+mig}^i + J_{n,elec}^i + \alpha^i - c_n^i \frac{dV_n}{dt} \right]$$

$$\frac{dc_n^{H^+}}{dt} = \frac{1}{V_n} \left[ J_{mig}^{H^+} + J_{n,elec}^{H^+} - c_n^{H^+} \frac{dV_n}{dt} \right]$$

# Modeling

## Determination of the electrochemical net mass fluxes: partitioning of the applied current

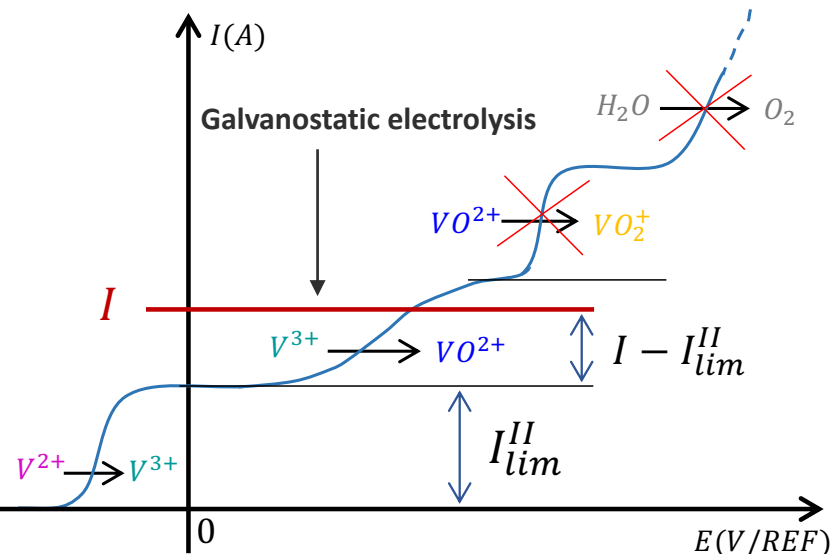
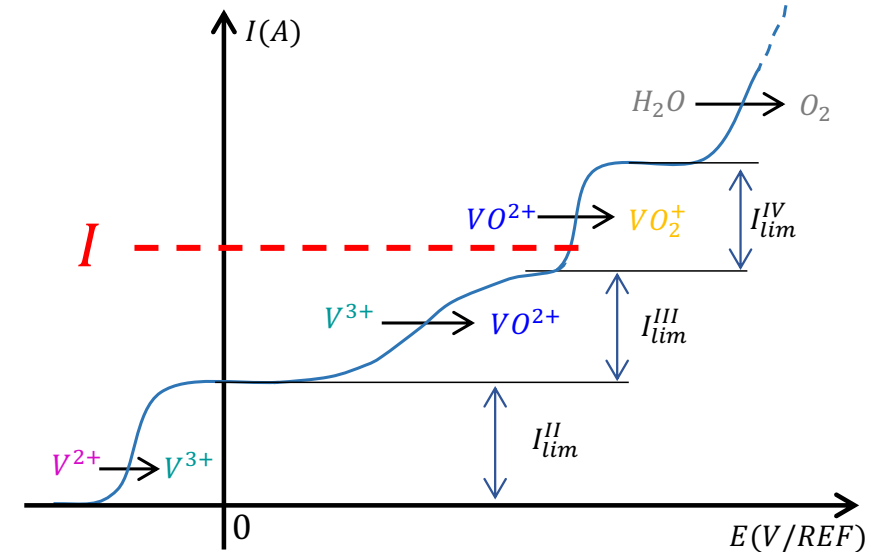
$$J_{p/n,elec}^i = (\text{production of } i) - (\text{consumption of } i)$$

→ Comparison between  $I$  Vs  $I_{lim}^i = Fk_c^i S c^i$

↙ Electrode surface area  
↘ Mass transfer coefficient

Example: posolyte side (oxidation) :

$$I_{lim}^{II} < I < I_{lim}^{II} + I_{lim}^{III}$$



Consumption of V(II) =  $k_c^{II} S c^{II}$   
 Consumption of V(III) =  $[I - Fk_c^{II} S c^{II}]/F$   
 Consumption of V(IV) = 0

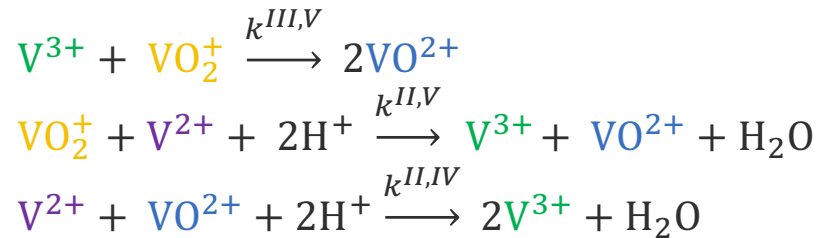
Production of V(III) =  $k_c^{II} S c^{II}$   
 Production of V(IV) =  $[I - Fk_c^{II} S c^{II}]/F$   
 Production of V(V) = 0

→ Development of an algorithm based on logical tests to compute  $J_{p/n,elec}^i$  at each step of the numerical calculation

$$\frac{dc_p^i}{dt} = \frac{1}{V_p} \left[ -J_{diff+mig}^i + J_{p,elec}^i + \alpha^i - c_p^i \frac{dV_p}{dt} \right]$$



## Determination of net mass flux due to the self-discharge reactions: $\alpha^i$



Reaction rates  $r_{i,j} = k^{i,j} \cdot c_i c_j \cdot V_p/n$

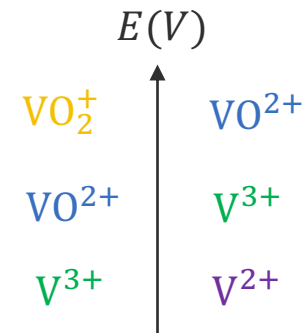
Taking into account all the contributions to compute  $\alpha^i$

$$\alpha^{II} = -r_{II,IV} - r_{II,V}$$

$$\alpha^{III} = -r_{III,V} + 2r_{II,IV} + r_{II,V}$$

$$\alpha^{IV} = 2r_{III,V} - r_{II,IV} + r_{II,V}$$

$$\alpha^V = -r_{III,V} - r_{II,V}$$

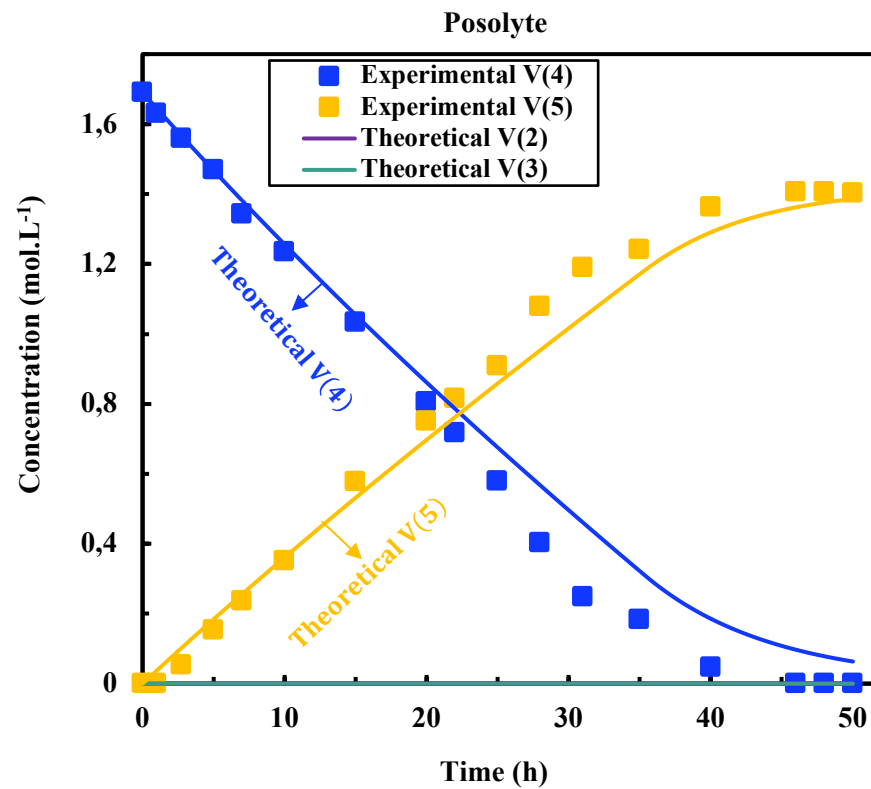
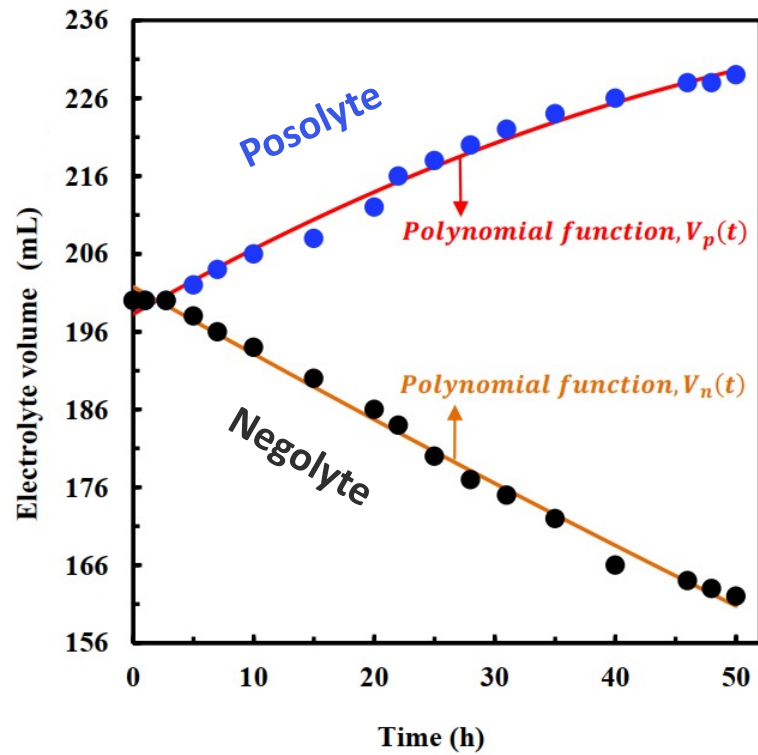


$$\alpha^i = f_i(c_{II}, c_{III}, c_{IV}, c_V)$$

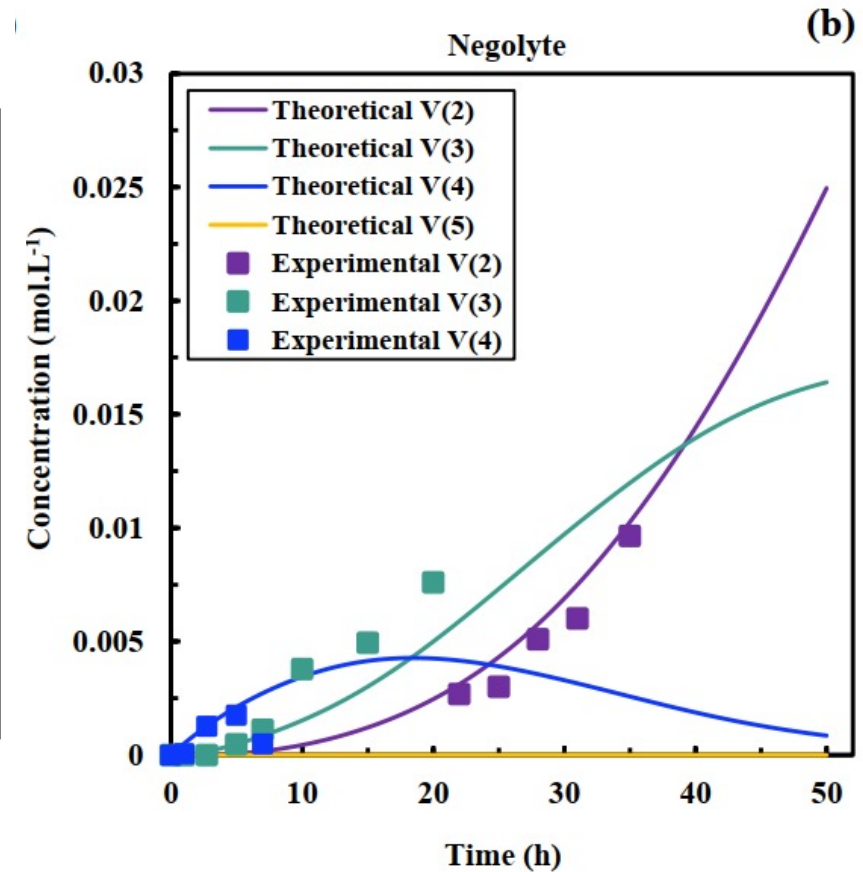
and the self-discharge reactions are assumed instantaneous (sufficiently high value of  $k^{i,j}$ )

$$\frac{dc_p^i}{dt} = \frac{1}{V_p} \left[ -J_{diff+mig}^i + J_{p,elec}^i + \alpha^i - c_p^i \frac{dV_p}{dt} \right]$$

# Experiments Vs Model prediction : Vanadium species

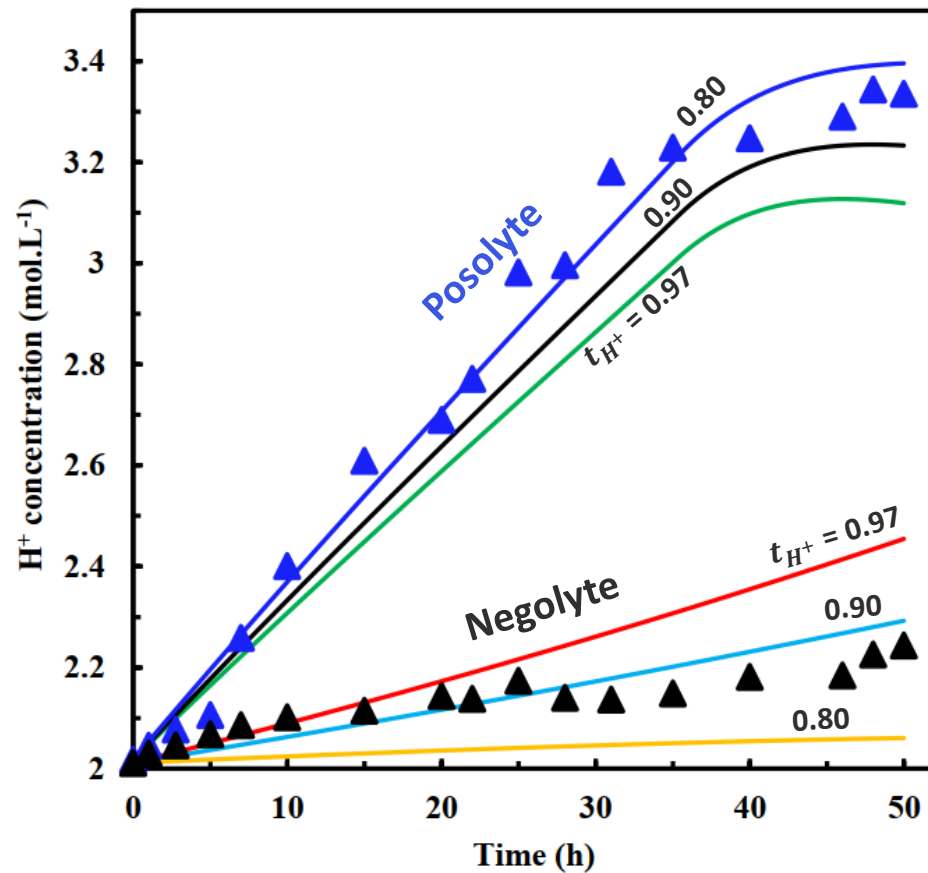
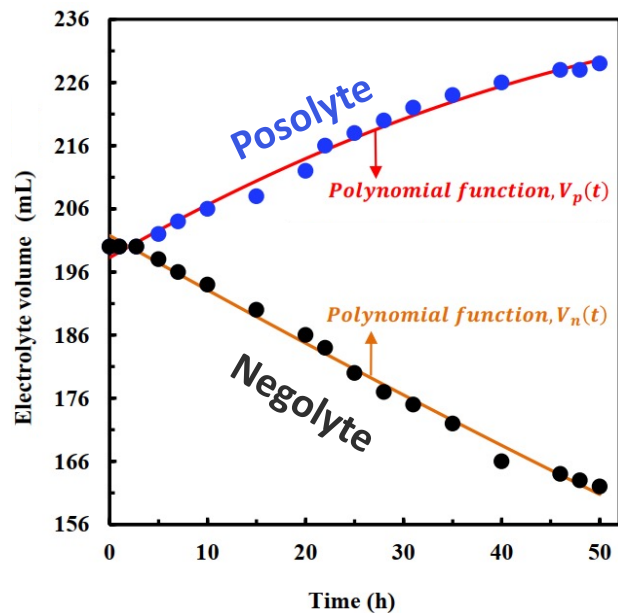


Good agreement ✓

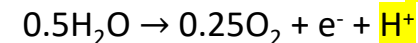


No V(V) detected ✓  
Good agreement except for V(IV)

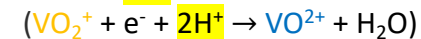
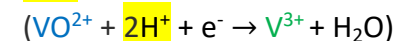
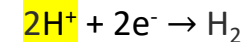
# Experiments Vs Model prediction : protons



At the positive electrode:



At the negative electrode:



Need to consider lower proton transfer number to match model to experiments

(explained by the non-negligible concentrations of cationic vanadium species compared to protons)

$$\frac{dc_p^{H^+}}{dt} = \frac{1}{V_p} \left[ -J_{mig}^{H^+} + J_{p,elec}^{H^+} - c_p^{H^+} \frac{dV_p}{dt} \right]$$

$$\frac{dc_n^{H^+}}{dt} = \frac{1}{V_n} \left[ J_{mig}^{H^+} + J_{n,elec}^{H^+} - c_n^{H^+} \frac{dV_n}{dt} \right]$$

$$J_{mig}^{H^+} = \frac{t^{H^+} I}{F}$$

# Conclusions

- Construction of a model to predict the temporal evolution of electrolyte composition taking into account:
  - the transport of V species and  $H^+$  in the membrane
  - the transfer of water
  - the partitioning of the applied current
  - the self-discharge reactions.
- Satisfactory agreement with experiments → coupling of main mass transport ph. with chemical & electrochemical reactions ✓
  - Improvement of the transport model inside the membrane (convection, electro-osmosis, osmosis, cations & anions, Donnan equilibrium, etc.) & Eq. for concentrated solutions, especially for higher current densities
- Future application to a real VRFB (V(IV)/V(V) | V(II)/V(III)) during charge/discharge cycles
  - To predict the energy loss coming from vanadium cross-over
  - To predict the temporal evolution of acid concentration

## More information:

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