Institut de Robòtica i Informàtica Industrial

CSIC

UNIVERSITAT POLITÈCNICA DE CATALUNYA BARCELONATECH

PhDday 2024

Monitoring and optimal operation of vanadium redox flow batteries

Author: Thomas Paul Puleston

Supervisors: Maria Serra Prat and Ramon Costa Castelló

System description

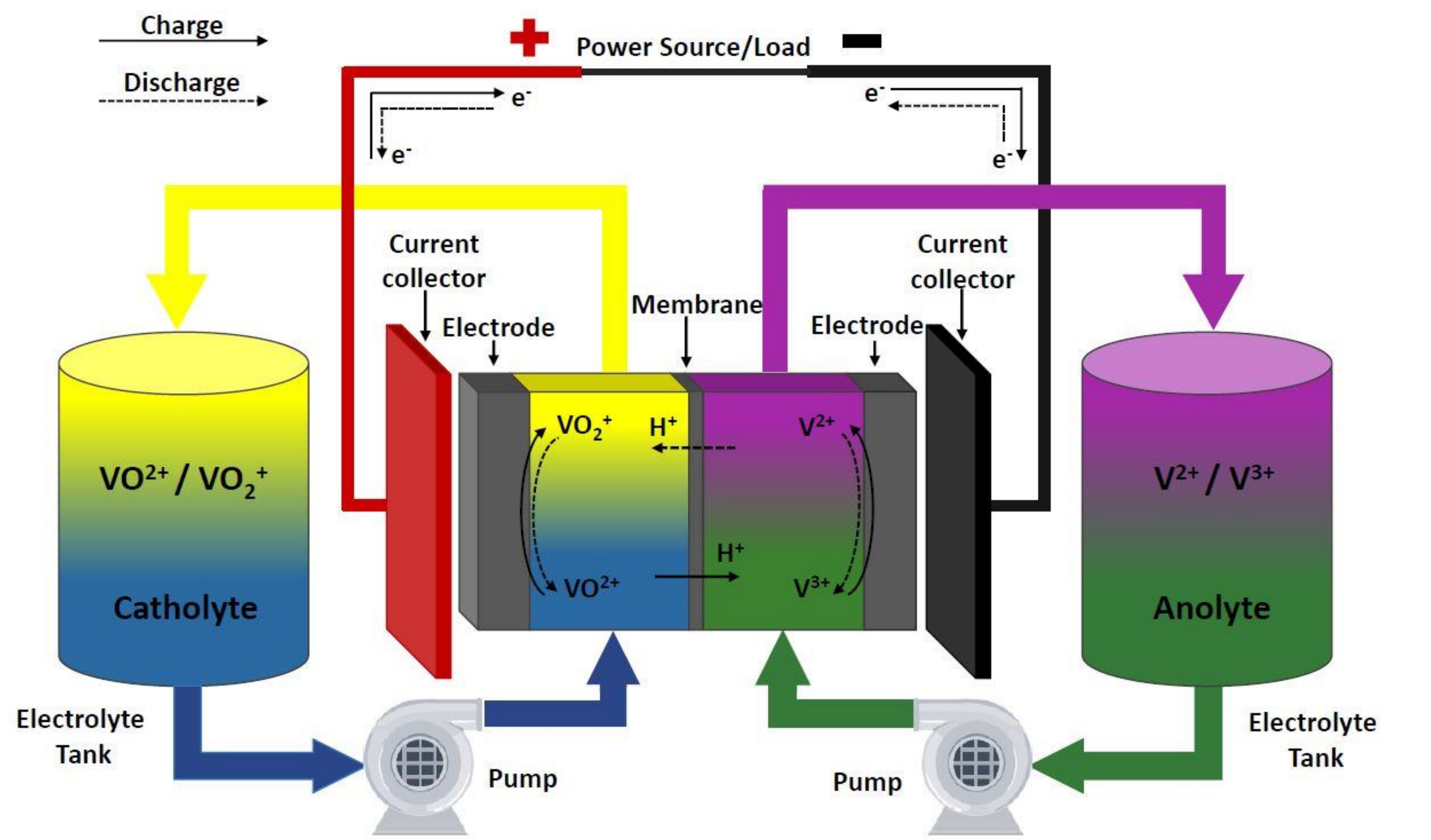

Fig. 1. Schematic illustration of a vanadium redox flow battery and its main components.

Vanadium redox flow batteries (VRFB) are a promising technolgy for large-scale stationary energy storage. The energy is provided by a reversible electrochemical reaction between vanadium ions with different oxidation states:

At the negative electrode: $$V^{2+} \underset{charge}{\overset{discharge}{\rightleftharpoons}} V^{3+} + e^-$$

At the positive electrode: $$VO_2^+ + 2H^+ + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} VO^{2+} + H_2O$$

Thesis objectives

1. To design **observers and parameter estimation strategies** to obtain information of unmesurable variables, such as the vanadium species concentrations, the State of Charge, the State of Health and electrochemical parameters.
2. To design **control setups** oriented to maximise the energy efficiency of the VRFB, mitigate the capacity loss associated **to side reactions and electrolyte imbalance**, and minimise the degradation of its components.
3. To develop enhanced control/estimation setups for augmented plants, considering the role of the VRFB as a part of **a hybrid energy system**, such as a renewable energy based electric vehicle charging station, or a dual redox flow battery for H_2 production.

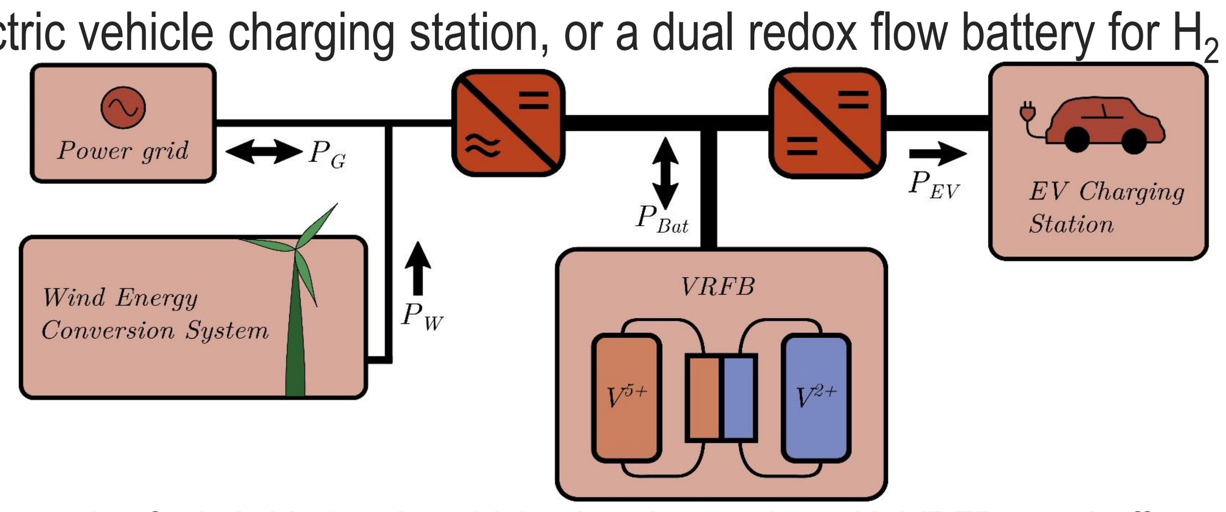

Fig. 2. Schematic of a hybrid electric vehicle charging station with VRFB as a buffer module.

Methodology

A. We use an electrochemical model to describe the system dynamics.

Vanadium species balances (i=2,3,4,5):

In the cells: $$\underbrace{V_c \frac{dc_i^c}{dt}}_{\text{Net accumulation}} = \underbrace{\frac{q}{n}(c_i^t - c_i^c)}_{\text{Inlet/outlet}} - \underbrace{\sum_{j=2}^{5} \alpha_{i,j} N_j}_{\text{Active species crossover}} + \underbrace{I/F}_{\text{Electrochemical reaction}}$$

In the tanks: $$\underbrace{V_t \frac{dc_i^t}{dt}}_{\text{Net accumulation}} = \underbrace{q(c_i^c - c_i^t)}_{\text{Inlet/outlet}} - \underbrace{\alpha_i c_i^t}_{\text{Tank side reactions (e.g. oxidation of } V^{2+})}$$

Cell voltage:

$$E_{cell} = E_{cell}^{oc} + \text{sign}(I) \cdot \underbrace{(|\eta_{ohm}| + |\eta_{act}| + |\eta_{con}|)}_{\text{Voltage losses}} \quad ; \quad \underbrace{E_{cell}^{oc} = E^0 + \frac{RT}{F} \ln\left[\left(\frac{c_2^c c_5^c c_H^2}{c_3^c c_4^c}\right)\left(\frac{\gamma_2 \gamma_5 \gamma_H^2}{\gamma_3 \gamma_4}\right)\right]}_{\text{Open circuit voltage}}$$

B. We use non linear observers to estimate the states that cannot be directly measured. The objective is to guarantee that the state estimates ($\hat{\mathbf{x}}$) converge to the real ones ($\mathbf{x}$) : $\lim_{t \to \infty} |\mathbf{x}(t) - \hat{\mathbf{x}}(t)| = 0$

E.g., metric-based observer with flow redesign for concentration estimation:

$$\dot{\hat{\mathbf{x}}} = \underbrace{f(\hat{\mathbf{x}}, u)}_{\text{Concentration dynamics}} + \underbrace{g(\hat{\mathbf{x}}, y, u)}_{\text{Correction term (guarantees convergence)}} + \underbrace{\mathbf{M}(\hat{\mathbf{x}})}_{\text{Flow redesign factor (physical constraints)}}$$

$$y := \text{measured voltage} \qquad \mathbf{x} := [c_2^c \; c_3^c \; c_4^c \; c_5^c \; c_2^t \; c_3^t \; c_4^t \; c_5^t]^T$$

C. The estimated variables can be used to monitor the battery status. Currently, we are also using them to develop enhanced control and optimization strategies.

Results

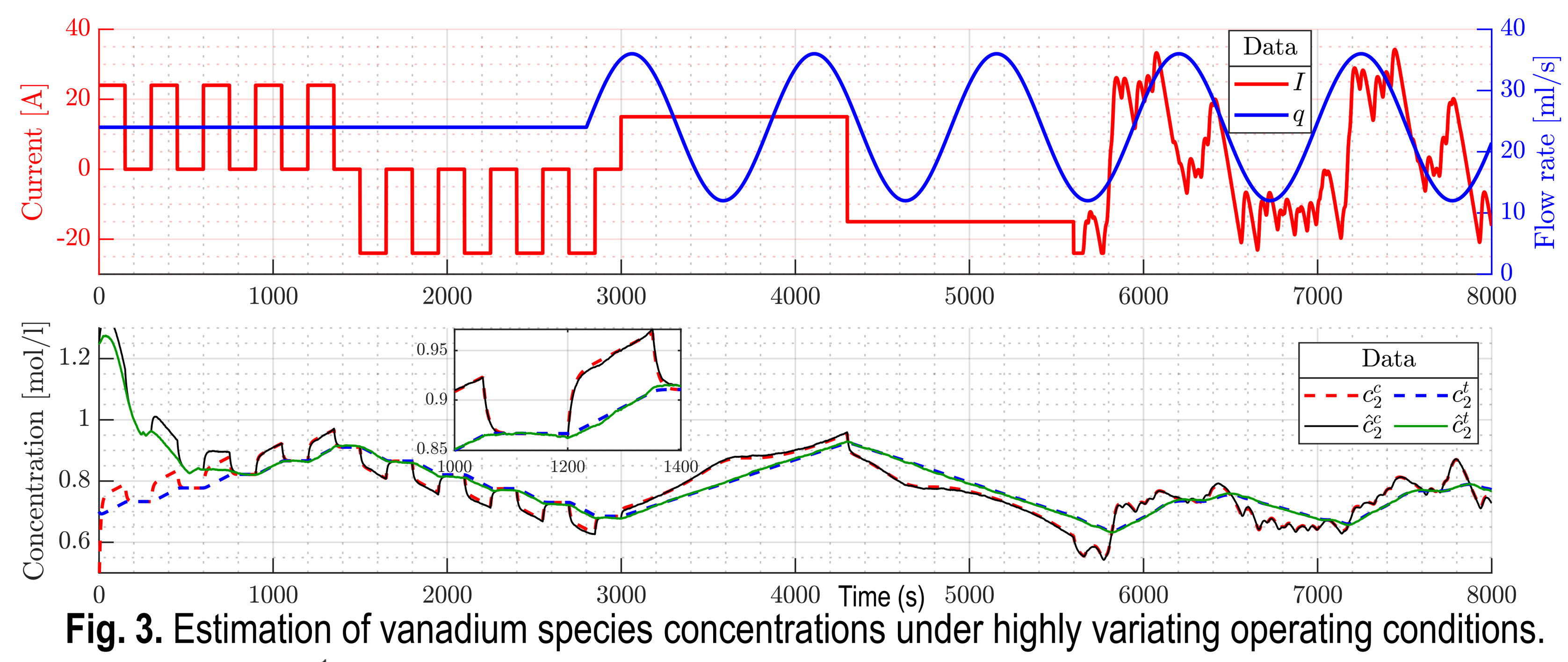

Fig. 3. Estimation of vanadium species concentrations under highly variating operating conditions.

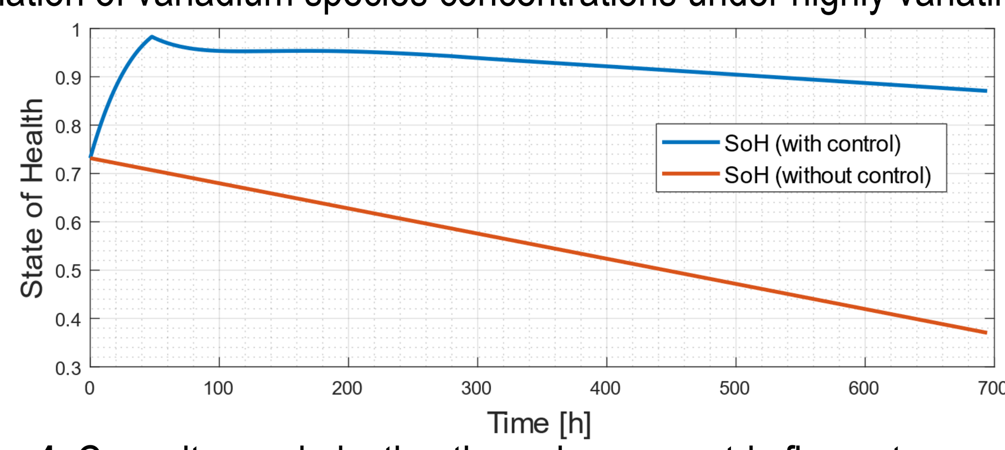

Fig. 4. Capacity maximisation through asymmetric flow rate regulation.

Start date: 20/10/2021

Thesis Project defense: 13/07/2022

Research collaborations and research stays

Research collaboration with LEICI Institute, Universidad Nacional de La Plata, Argentina.

Research stay in 2023 in EESCoLab Institute, University of Padova, Italy.

Funding

Grant la Caixa INPhINIT Incoming, funded by "la Caixa" Foundation.

"la Caixa" Foundation

Publications

T. Puleston, G. Marini, A. Trovò, M. Serra, R. Costa-Castelló, M. Guarnieri. **Design and experimental validation of an optimal remixing procedure for vanadium flow batteries affected by faradaic imbalance.** Journal of Power Sources (under review), 2024.

T. Puleston, A. Cecilia, R. Costa-Castelló, M. Serra. **Nonlinear observer for online concentration estimation in vanadium flow batteries based on half-cell voltage measurements .** Computers and Chemical Engineering, 2024.

T. Puleston, M. Serra, R. Costa-Castelló. **Vanadium redox flow battery capacity loss mitigation strategy based on a comprehensive analysis of electrolyte imbalance effects.** Applied Energy, 2023.

T. Puleston, A. Cecilia, R. Costa-Castelló, M. Serra. **Vanadium redox flow batteries real-time State of Charge and State of Health estimation under electrolyte imbalance condition.** Journal of Energy Storage, 2023.

P. Fornaro, T. Puleston, P. Puleston, M. Serra, R. Costa-Castelló, P. Battaiotto. **Redox flow battery time-varying parameter estimation based on high-order sliding mode differentiators.** International Journal of Energy Research, 2022.