



# Local potential measurement through reference electrodes in vanadium redox flow batteries: Evaluation of overpotentials and electrolytes imbalance



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## HIGHLIGHTS

- We applied through-plate reference electrodes at electrodes inlet and outlet of a VRFB.
- Negative electrode is kinetically dominated and the positive is mass transport limited.
- Electrodes OCP trends reveal electrolytes imbalance during cycling.
- Cross-contamination mainly affects the negative electrolyte.

## ARTICLE INFO

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## ABSTRACT

Vanadium redox flow battery performance is actually hindered by increased overpotentials at high current, due to poor electrochemical activity of the most commonly used carbon electrodes and to electrolyte distribution, implying local mass transport limiting conditions. Moreover, vanadium cross-contamination leads to coulombic efficiency reduction and uncontrolled electrolytes imbalance. This work presents the application of through-plate reference electrodes at inlet and outlet of both positive and negative electrodes. The utility of the electrodes potential measurement is firstly demonstrated in the identification of a relation between electrolytes potential and the corresponding state of charge. Subsequently, local overpotentials and impedance spectra at both electrodes are evaluated, evidencing that the negative electrode is kinetically dominated and presents high overpotential even at low current, while the positive exhibits mass transport effects at high current, especially at cell outlet. Finally, during cycling operation with fixed capacity reference electrode measurements permit to monitor electrolytes imbalance induced by cross-contamination, that mainly affects negative electrolyte. Moreover, additional insights into electrodes potential loss during cycling are provided.

## 1. Introduction

Vanadium redox flow battery (VRFB) is a promising technology for energy storage due to its peculiarity to separate power and energy, its high efficiency and extremely long charge/discharge cycle life [1–4]. However, the commercialization of VRFB continues to be hindered by technological issues, among which low specific surface area and poor electrochemical activity of the most commonly used carbon materials [5] and the mass transport of the electrolyte over the porous electrode [4,6], leading to increased overpotential at high current and limited system power density [7,8]. Moreover, even though VRFB employs the same element in different oxidation states in both electrolytes, vanadium cross-over induces side reactions [9] and leads to an undesired

variation of electrolyte state of charge (SoC), that occurs with a different intensity at the two half-cell, implying electrolyte imbalance and battery capacity loss [9,10].

The quantification of electrodes overpotential and electrolytes SoC is fundamental for VRFB improvement and components optimization; thus, the development of local and reliable reference electrodes becomes crucial to address these critical issues. Additionally, during system lifetime local potential measurements can reveal which region of the cell is undergoing severe degradation or working in limiting condition, providing useful insights on the adoption of suitable operating strategy and components replacement.

In the literature only limited effort has been dedicated to the development of reference electrode in VRFB; the most of the works

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[11–14] report the application of dynamic hydrogen electrodes (DHE) in both *sandwich type* or *edge type* configuration. The former is a platinum wire inserted between two membranes, altering cell performance, while the latter is a platinum wire applied on the border of the membrane outside the area defined by the electrode, introducing edge effects in the measurement.

Aaron et al. [11] inserted a DHE between two Nafion® membranes and observed higher potential loss at the negative electrode. In Ref. [15] individual electrode impedance were performed and the spectra derived from the negative exhibited high-frequency semi-circular features that were ascribed to a process limited by kinetic. In Ref. [12] DHE was used to study half-cell reactions in a vanadium-air battery, highlighting that the cathodic reaction limits system efficiency. In Ref. [13] DHE with resistor design was coupled with galvanostatic intermittent titration technique to determine the equilibrium electrode potential for both electrodes, providing a deeper understanding of the observed double-step OCV decay. However, in these works [11–13] no local information about the distribution of electrodes potential and the corresponding impedance spectra were provided.

Mench et al. [16] first developed an experimental method for the measurement of local potential within a multi-layered electrode at the positive side of VRFB. Through-plane potential measurements permitted the evaluation of vanadium concentration and the location of reaction, indicating a mass transfer limited situation with increasing current density.

C. Roth et al. [17] placed in the inlet and outlet tubing of a VRFB two Ag/AgCl reference electrodes, working as Luggin capillaries. The measured voltages between the reference electrodes and the half-cell electrode were used to compare the performance of pristine and thermally oxidized carbon felts at both negative and positive electrodes. In a recent work [18], a similar set-up was adopted to analyze electrode degradation during cycling with different cut-off voltages. However, the Ag/AgCl reference electrode set-up [17,18] does not permit the measurement of actual electrodes potential.

In this work, the system of through-plate reference hydrogen electrodes already proposed by NPL for polymer electrolyte fuel cell is adopted [19] and locally applied in-plane to VRFB. It consists in salt bridges passing through the end plates of the cell, creating an ionic contact between the electrode and a reference hydrogen electrode placed outside the cell. This configuration permits the local measurement of electrolytic potential [19]. In Ref. [14], one single through-plate reference electrode was already applied to evaluate potential loss in a regenerative hydrogen-vanadium fuel cell, but only OCV condition was analysed with electrochemical impedance spectroscopy.

In this work, through-plate reference electrodes are introduced at inlet and outlet of both positive and negative VRFB electrodes, providing an insight into the evaluation of local overpotentials, electrolyte imbalance and electrodes potential loss during system cycling.

## 2. Experimental

### 2.1. Experimental setup

The cell active area was 25 cm<sup>2</sup> with single serpentine graphite distributors. The membrane was Nafion® 115 and both positive and negative electrodes were SGL 39 AA carbon paper (nominal thickness of ~290 μm, compressed to 230 μm). The cell temperature was maintained at ambient temperature of 23 ± 2 °C. In the hydraulic circuit of each electrolyte a pulse dampener [20,21] was introduced to get rid of flow rate fluctuations induced by the peristaltic pump (Watson-Marlow 323Du with a 314Dw 4 roller headpump). A potentiostat (Material Mates 350-R, current range 10 A/-30 A, voltage range -12 V/+12 V) was used to perform polarization curves and cycling, while electrodes impedance spectra were recorded with a potentiostat (Autolab PGSTAT 30<sup>+</sup>) equipped with a frequency response analyzer module.

The positive and negative electrolyte solutions were prepared

according to the procedure reported in Ref. [22], starting from a mixture of 1 M vanadium IV sulfate oxide hydrate (Alfa Aesar) and 5 M sulfuric acid (Fischer Chemicals). The volume of each electrolyte was 300 ml in order to have a sufficient quantity of solution to perform polarization curves assuming a constant SoC. Additionally, the bottles containing the electrolyte were maintained pressurized with N<sub>2</sub> to avoid air infiltration.

### 2.2. Reference electrodes

The local reference electrode measurement setup, along with the related operating principle, has been extensively described in Ref. [19]. In this work it has been applied to VRFB and it consisted in a Nafion® tube salt bridge (diameter 0.64 mm) inside a protective PTFE tubing (diameter 0.84 mm). The salt bridge was saturated with 5 M sulfuric acid to guarantee the necessary proton conductivity and to directly connect the surface of VRFB working electrode with a 5 M sulfuric acid electrolyte solution, in which a Gaskatel HydroFlex® reversible hydrogen electrode (RHE) was immersed. In order to provide an insight into local VRFB performance and electrolytes imbalance, two measurement points were introduced at both positive and negative electrode, close to the inlet and the outlet of cell active area. A schematic of the experimental set-up is reported in Fig. 1.

### 2.3. Experimental tests

#### 2.3.1. Relation between potential measurements and SoC

In the literature VRFB models showed discrepancies with experiments in the evaluation of open circuit voltage (OCV) [23], resulting in imprecise relations between OCV and battery SoC [24]. Moreover all the presented models were validated with respect to cell OCV, implying possible inaccuracies in the evaluation of negative and positive electrolytes SoC. In this work, since positive and negative electrode open circuit potential<sup>1</sup> (OCP) were measured, an experimental relation between electrodes OCP and the corresponding electrolyte SoC was adopted. These relations were obtained starting from a fully discharged battery: in this condition the negative and positive electrolytes are respectively composed by vanadium ions V<sup>3+</sup> and VO<sup>2+</sup> and the measured electrodes OCP corresponds to SoC 0%. Then the battery was charged in multiple steps at fixed capacity (725 C) and electrodes OCP was monitored until the charging current reached 5 mA at 1.8 V. In this condition the battery is fully charged and the measured electrodes OCP corresponds to SoC 100%. Afterwards it was thus possible to determine the relation between electrode potential and corresponding electrolyte SoC in the whole range of SoC.

#### 2.3.2. Polarization curves and impedance spectra

Polarization curves were performed in galvanostatic mode following one-way curve increasing the current density by steps of 0.05 A cm<sup>-2</sup>, with each step being held for 45 s, until one among positive and negative electrode potentials reached the limiting value of 0.5 V. In order to investigate a wide range of operating current densities, generally up to 0.55 A cm<sup>-2</sup>, polarization curves were measured only during discharge, since the charge was limited by hydrogen evolution at the negative electrode [25]. Even though the current density during normal charge-discharge cycles are considerably lower in order to obtain an energetic efficiency around 80%, polarization curves at high current density highlight the limiting phenomena and enhance the differences between cell inlet and outlet. The investigated operating conditions were SoC 50% at different flow rates: 10, 40 and 100 ml min<sup>-1</sup>. The positive and negative electrode overpotentials at cell inlet and outlet

<sup>1</sup> In open circuit, since the reaction overpotentials are null, the measured OCP at positive and negative electrode corresponds to the relative electrolyte potential.

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