# Measuring density and viscosity of vanadium electrolytes: An exhaustive database with multivariate polynomial fits

Pablo A. Prieto-Díaz<sup>a</sup>, Ange A. Maurice<sup>a</sup>, Marcos Vera<sup>a</sup>

<sup>a</sup>Departamento de Ingeniería Térmica y de Fluidos, Universidad Carlos III de Madrid, Avd. de la Universidad 30, Leganés, 28911, Madrid, Spain

# Abstract

The variation of the physical properties of vanadium electrolytes during vanadium redox flow batteries (VRFB) operation is known to have a significant impact on the flow of the electrolytes both in the cells and in the tanks. This study presents extensive accurate measurements of the density and viscosity of vanadium electrolytes for VRFBs spanning a four-dimensional parameter space, including State of Charge (SoC), total vanadium concentration, total sulfate concentration, and temperature. The experimental results reveal different trends in the density variations of the posolyte and negolyte. Specifically, while the density of the posolyte slightly increases with SoC, that of the negolyte decreases more significantly. Furthermore, temperature exerts a linear influence on the density of both electrolytes. The analysis also reveals complex and non-linear dependencies between viscosity and the parameters under study, with more pronounced variations being observed at higher vanadium concentrations. In particular, the viscosities of both electrolytes are seen to decrease with SoC, the viscosity of the negolyte being consistently higher than that of the posolyte. We also present multivariate regression fits accurately capturing the variations of electrolyte properties, aiming to provide valuable insights into the dynamic behavior of vanadium electrolytes and enable more accurate physics-based mathematical models.

*Keywords:* Vanadium redox flow batteries, Electrolyte properties, Density, Viscosity, Measurements, Multivariate regressions

## 1. Introduction

Redox Flow batteries (RFBs) stand out among other energy storage technologies due to their modular design and long cycle life [1]. Vanadium Redox Flow Batteries (VRFBs) are currently the market leaders, owing to the possible re-utilization and rebalancing of their electrolytes [2, 3]. However, they still need to boost their competitiveness, given their higher costs and lower overall performance compared to other energy storage technologies, such as lithium-ion batteries [4]. To improve the performance and operational flexibility of VRFBs, a comprehensive understanding of the electrolyte flow within the electrochemical conversion cell and the storage tanks is imperative. In particular, operational variations of electrolyte density and viscosity are known to affect VRFB operation.

*Email addresses:* pabloangel.prieto@uc3m.es (Pablo A. Prieto-Díaz), amaurice@pa.uc3m.es (Ange A. Maurice), marcos.vera@uc3m.es (Marcos Vera)

Density differences between the renewed and resident electrolyte give rise to buoyancy forces that affect the electrolyte fluid dynamics and mixing within the tanks, potentially leading to the formation of heterogeneous regions containing unreacted electrolyte, which reduces the VRFB capacity utilization [5]. Similarly, viscosity plays a pivotal role within the electrochemical cell, affecting ion mass transport fluxes and, consequently, the overall electrochemical performance [6, 7], as well as the pressure work. In summary, accurate density and viscosity data of vanadium electrolytes is necessary to improve mathematical models and optimize VRFB design.

Mousa [8] reported density measurements for the discharged negative electrolyte for varying total vanadium concentration, sulphates concentration and temperature. Later, Rahman et al. [9] measured the density of the positive electrolyte at 5 M vanadium concentration in 8 M sulphates concentration. Xu et al. [10] investigated the density and thermal expansion coefficient of VOSO<sub>4</sub>. Skyllas et al. [3] reported density data for both electrolytes, using 2 M vanadium concentrations in 5 M total sulphates for varying State of Charge (SoC) and temperature. However, they did not give any details regarding the experimental procedure nor provided error estimations. More recently, Ressel et al. [11] measured the density of the negative electrolyte as a function of SoC obtaining results that were consistent with those of Skyllas et al. [3]. Except for these two works, prior studies lack information regarding the variation of density with the SoC, a crucial parameter intrinsic to battery operation. Furthermore, a recent study by the authors has provided experimental evidence supporting previous density measurements of the negolyte, but suggesting potential overestimations in the density variations of the posolyte [12].

The viscosities of the posolyte and the negolyte are notably influenced by the total vanadium concentration and temperature [6, 8, 13]. Li et al. [14] compiled the most extensive database of viscosity values for varying SoC and temperature, using 1.6 M and 1.8 M vanadium concentration in 2.6 M and 2.7 M sulphuric acid solutions, respectively. However, this research did not include measurements for fully charged/discharged electrolytes, nor did it explore the combined influence of vanadium and sulphate concentrations.

In the referenced works, we hypothesize that a significant source of measurement error may come from the sample preparation methods. Previous research relied solely on electrochemical measurements and visual color cues to prepare solutions at specific SoCs, omitting more precise characterization techniques such as UV-Visible spectroscopy [15]. To summarise, the gaps in the literature call for open access, precise and extensive data regarding the physical properties of vanadium electrolytes, especially those describing their variations with the SoC. This paper aims to provide a comprehensive and accurate database containing density and viscosity values for both positive and negative electrolytes, measured at well defined compositions, while varying the relevant parameters, i.e., the SoC, total vanadium and sulfates concentrations, and temperature.

The work is structured as follows. First, we describe the measuring equipment, the experimental procedures and the protocols employed to prepare the electrolyte samples and measure their physical properties. In a second part, we present the density and viscosity data as well as their changes with all the aforementioned parameters. We also provide multivariate regression fits that capture the variation of the electrolyte properties in all parameter space. This paper comes with Supplementary Information materials, mainly describing the quantification of the sulfate and vanadium concentrations. The Supplementary Information also contains additional density and viscosity plots and details about the empirical regression of viscosity. Finally, as part of our open science commitment, we provide the raw density and viscosity data in csv format.

# 2. Methods

#### 2.1. Density and viscosity measurements

The densimeter is a DMA 4500 M (Anton Paar) that uses the oscillating U-tube principle (accuracy and repeatability  $5 \cdot 10^{-5}$  and  $5 \cdot 10^{-6}$  g/cm<sup>3</sup>, respectively). The viscometer is a Lovis 2000 ME (Anton Paar) falling ball micro-viscometer with 0.5% accuracy and 0.1% repeatability. The capillary diameter was 1.59 mm and a gold coated ball (1.5 mm diameter) was used to prevent corrosion. The two systems, coupled in series in the same equipment, include ThermoBalance<sup>m</sup> temperature management, which allows to quickly perform accurate measurements at different temperatures, guaranteeing long-term stability for temperature scans. Upon injecting the sample, the liquid fills both the densimeter and the viscometer simultaneously. Approximately 2 mL is needed to fill the system. The samples were 4 mL, injected via a 6 mL syringe. Between each measurement, the cavities were purged injecting solvents in the following order: water-drying-acetone-drying. Deionized water was used to dilute and evacuate vanadium compounds whilst acetone was used to evacuate water for fast drying. We performed repeatability measurements to ensure that this cleaning protocol matched the values given by the manufacturer. Additionally, we regularly checked the densimeter and viscometer calibrations, ensuring that there was no remaining residue inside the system.

#### 2.2. Sample preparation

We generated the samples of desired composition via pipetting previously prepared reference solutions of vanadium electrolytes, sulfuric acid and water with phosphoric acid. For the negolyte, we mixed  $V^{2+}$  and  $V^{3+}$  ( $V^{\parallel}/V^{\parallel}$ ) and, for the posolyte,  $VO^{2+}$  and  $VO_2^+$  ( $V^{\parallel}/V^{\vee}$ ). The pipettes were calibrated using deionized water and a scale, yielding 0.3% repeatability and 0.45% accuracy. We prepared the reference solutions via electrochemical charge/discharge from an initial equimolar V<sup>III</sup>/V<sup>IV</sup> commercial solution (Oxkem Limited, UK). The electrolyte data sheet was provided with, a vanadium, sulfuric acid and phosphoric acid concentration of, respectively, 1.8 M, 4.6 M, and 0.05 M. However, we deemed these values unreliable for our study since the commercial datasheet indicated a 10% error in the vanadium and sulfate concentrations. In particular, the density of 98%sulfuric acid is  $1.83 \text{ g/cm}^3$ . Thus, we expect the concentration (ca. 22% in weight) of sulfuric acid to have a significant impact on the density measurements. For these reasons, we determined the sulfate, phosphate and vanadium concentration of our starting electrolyte, whose exact composition is listed in Table 1. We quantified the sulfate concentration using the procedure outlined in Oreiro et al. [16], based on the precipitation of sulfate ions and barium ions as well as precise density measurement. We measured the total vanadium concentration via spectrophotometric titration of  $VO_2^{2+}$ , oxidized by potassium permanganate (KMnO<sub>4</sub>). The phosphoric acid concentration was measured by induction coupled plasma-optical emission spectroscopy (ICP-OES). Details regarding these procedures are given in the Supplementary Information. Additional information regarding the electrochemical preparation is described in our recent paper by Maurice et al. [15]. It is worth noting that the reference V<sup>II</sup> solutions were degassed before pipetting, as during the charge of the negolyte some diluted hydrogen appears because of the electrolysis of water.

Species	Concentration
Vanadium	$1.830\pm0.02~\mathrm{M}$
Sulfuric Acid	$4.07\pm0.03~\mathrm{M}$
Phosphoric Acid	$0.0409 \pm 0.0024~{\rm M}$
Oxidation number	$\approx +3.5$

Table 1: Composition of the equimolar  $V^{III}/V^{IV}$  commercial vanadium electrolyte (Oxkem Limited, UK) used as starting point in the study, with an average oxidation number of +3.5.

#### 3. Results and discussion

This section describes the data obtained with the procedure outlined above for measuring the electrolytes density and viscosity, while varying the State of Charge, SoC, total vanadium concentration,  $c_{\rm V}$ , and sulphates concentration,  $c_{\rm S}$ . We prepared four sample groups with  $c_{\rm V} =$ (1.830, 1.525, 1.220, 0.915) M while keeping  $c_{\rm S} = 4.07$  M constant. In addition, we prepared three additional groups with  $c_{\rm S} = (3.40, 2.80, 2.20)$  M and  $c_{\rm V} = 0.915$  M constant. For each sample group, we prepared six dilutions varying the SoC = (0, 0.2, 0.4, 0.6, 0.8, 1). The density and viscosity of these samples were measured at three temperatures  $T = (10, 20, 30)^{\circ}$ C. Furthermore, we added 10 randomised samples with arbitrary values of the four parameters chosen within their respective evaluated range. The measurement points, with their respective parameter values and density and viscosity measurements, were collected in a separate csv format file that is freely available as indicated in the data availability section. It is important to note that in the main sample groups we varied only  $c_{\rm V}$  while keeping  $c_{\rm S}$  constant, or vice versa. This prevented the observation of the effect of simultaneous changes in both  $c_{\rm V}$  and  $c_{\rm S}$ . The random samples enabled us to capture the collective influence of all parameters at once, therefore improving the precision of the fit. Accounting for the posolyte and negolyte, the number of samples doubled to a total of 272 measurement points.

To enable the use of raw laboratory data in studies requiring the assessment of local electrolyte properties, the density and viscosity measurements were subjected to polynomial fitting using multivariable regression techniques. Below, regressions for the density,  $\rho^j$ , and viscosity,  $\nu^j$ , of both electrolytes,  $j = \{+, -\}$ , are presented and discussed. The regressions are conveniently expressed as Taylor series centered around the reference values  $c_{V,0} = 0.915$  M,  $c_{S,0} = 2.20$  M,  $T_0 = 10^{\circ}$ C, and SoC = 0 facilitating the isolation of the effects of various parameters in distinct terms. During the derivation of the polynomial fits, terms with coefficients significantly smaller than others were neglected.

## 3.1. Density

The density of the posolyte and the negolyte is assumed to depend on the species concentrations (i.e., total vanadium and sulphate concentrations,  $c_{\rm V}$  and  $c_{\rm S}$ , and SoC) as well as the electrolyte temperature following the functional dependence

$$\rho^{j} = \rho_{0}^{j} + \rho_{T}^{j} \left( T - T_{0} \right) + \rho_{\text{SoC}}^{j} \text{SoC} \quad \text{for} \quad j = \{+, -\}$$
(1)

where

$$\rho_0^j = A^j + B^j \left( c_{\rm V} - c_{\rm V,0} \right) + C^j \left( c_{\rm S} - c_{\rm S,0} \right) + D^j \left( c_{\rm V} - c_{\rm V,0} \right)^2 + E^j \left( c_{\rm S} - c_{\rm S,0} \right)^2 \tag{2}$$

represents the density of the discharged electrolyte,  $\rho_0^j \equiv \rho_0^j (c_V, c_S, T_0, \text{SoC} = 0)$ , at the reference temperature  $T_0$  and the specified total vanadium and sulphate concentrations. These expressions assume that the electrolyte density varies linearly with T and SoC, but quadratically with the total vanadium and sulphate concentrations. As a result,  $\rho_T^j = (\partial \rho^j / \partial T)_{\text{SoC}^j}$  and  $\rho_{\text{SoC}}^j = (\partial \rho^j / \partial \text{SoC})_{T^j}$ denote the partial derivatives of  $\rho^j$  with respect to T and SoC,  $A_j$  is the density at the reference state  $(c_{V,0}, c_{S,0}, T_0, \text{SoC} = 0)$ , and  $B^j$  to  $E^j$  represent the linear and quadratic fitting coefficients for the density variations with the total vanadium and sulphate concentrations. Density is thus expressed as the density  $\rho_0^j$  of the discharged electrolyte at a given temperature and composition (2) plus its variations with the SoC and temperature during VRFB operation (1). The multivariate regression coefficients obtained from the experimental campaign are listed in Table 2. The regression for  $\rho^+$ yielded a root mean squared error (RMSE) of  $7.80 \cdot 10^{-4} \text{ g/cm}^3$ , while that for  $\rho^-$  gave a RMSE of  $9.10 \cdot 10^{-4} \text{ g/cm}^3$ .

Coef.	$ ho^+$	$ ho^-$	Unit
$A^j$	1.217	1.218	${\rm g~cm^{-3}}$
$B^{j}$	$6.93\cdot10^{-2}$	$7.08 \cdot 10^{-2}$	$\mathrm{g~cm^{-3}~M^{-1}}$
$C^{j}$	$6.23\cdot10^{-2}$	$6.02 \cdot 10^{-2}$	$\mathrm{g~cm^{-3}~M^{-1}}$
$D^{j}$	$-1.89 \cdot 10^{-3}$	$-5.93\cdot10^{-3}$	${\rm g}~{\rm cm}^{-3}~{\rm M}^{-2}$
$E^{j}$	$-2.68\cdot10^{-3}$	$-1.64 \cdot 10^{-3}$	${\rm g}~{\rm cm}^{-3}~{\rm M}^{-2}$
$ ho_T^j$	$-7.04\cdot10^{-4}$	$-6.63 \cdot 10^{-4}$	$\mathrm{g~cm^{-3}~K^{-1}}$
$ ho_{ m SoC}^j$	$2.73\cdot 10^{-3}$	$-(1.30+1.46(c_{\rm V}-c_{\rm V,0}))\cdot 10^{-2}$	${\rm g~cm^{-3}}$

Table 2: Multivariate regression coefficients for the density functions (1) and (2) of both electrolytes.

Figure 1 shows the density of the posolyte (left) and negolyte (right) as a function of SoC for different temperatures and total vanadium concentrations. In all cases, the measurements (symbols) follow linear trends as highlighted by the empirical regressions (dotted lines). The density of the posolyte shows a slight increment with SoC, with  $\rho_{SoC}^+ = 2.73 \cdot 10^{-3} \text{ g cm}^{-3} > 0$ , independent from  $c_V$ . The experimental results suggest a slight reduction in  $\rho_{SoC}^+$  with decreasing  $c_V$ . But the reduction is so weak that it cannot be accurately captured thorugh regression fitting, as it falls within the same order of magnitude as the estimated error. Regarding the temperature dependence, the posolyte density is seen to decrease linearly with T, the value of  $\rho_T^+$  remaining virtually independent across all parameter space. In the context of VRFB operation, during charge the density of the posolyte should slightly increase due to the SoC increment, but, as the temperature tends to decrease [17], the overall density variation could be roughly cancelled. Since these effects are known to reverse during discharge, the posolyte should therefore show negligible density variations during the entire charge/discharge cycle.

By way of contrast, the density of the negolyte exhibits a notable reduction with SoC, leading to a considerably larger (absolute) value of  $\rho_{SoC}^- = -(1.30 + 1.46 (c_V - c_{V,0})) \cdot 10^{-2} \text{ g cm}^{-3}$  that grows with  $c_V$ . These density variations are relevant for VRFB operation, as they have the potential of affecting the fluid dynamics of mixing in the negative tank [5]. The resulting buoyancy induced flows cause the renewed electrolyte to either rise or sink upon discharge in the tank, with a direct impact on capacity utilization confirmed in recent work [12]. Moreover, the value of  $\rho_T^-$  is similar to that of the posolyte, and it also exhibits negligible variations with electrolyte composition.



Figure 1: Density of the posolyte (left) and negolyte (right) electrolyte versus SoC for  $T = (10, 20, 30)^{\circ}$ C,  $c_{\rm V} = (0.915, 1.220, 1.525, 1.830)$  M, and  $c_{\rm S} = 4.07$  M. Symbols: measurements; lines: empirical regressions (1)-(2).

The sulfate concentration does not interact with other parameters and only affects the term  $\rho_0^j$  reflecting the dependence on the composition of the discharged electrolyte. Figure 2 shows contour plots of  $\rho_0^+$  (top) and  $\rho_0^-$  (bottom) in the range of vanadium and sulphates concentrations under study, highlighting the position of the measurement points in the  $(c_V, c_S)$  plane. As seen in Table 1, the two electrolytes have very similar values of the coefficients  $A^j - E^j$ , so the maps of  $\rho_0^j$  are almost indistinguishable to the naked eye. In summary, the value of  $\rho_0^j$  is fundamentally determined by the parameters  $c_V$  and  $c_S$ , which are independent of each other, and for given values of these parameters it is practically independent of the electrolyte.

The region labeled as *unexplored* in Figure 2 corresponds to values of vanadium and sulfate concentrations that have not been addressed in this study. Thus, while our empirical regression yields reasonably accurate values within the parametric range examined, its predictions will be increasingly less precise the further we go into the uncharted region.

#### 3.2. Viscosity

Figure 3 shows the viscosity of the posolyte (left) and the negolyte (right) plotted versus the SoC for various total vanadium concentrations at  $T = 20^{\circ}$ C and  $c_{\rm S} = 4.07$  M. Hereafter all results will be presented in terms of kinematic viscosity. As seen in the figure, both electrolytes exhibit the same behavior: the viscosity increases with vanadium concentration but decreases with SoC. The negolyte exhibits higher viscosities (5.82, mm<sup>2</sup>/s) compared to the posolyte (4.55, mm<sup>2</sup>/s), along with a more pronounced interaction between vanadium concentration and SoC, characterized by a nonlinear dependence that decreases for increasing values of  $c_{\rm V}$ .



Figure 2: Contour plots of  $\rho_0^+$  (top) and  $\rho_0^-$  (bottom) in the range of vanadium and sulphates concentrations under study. The measurement points are marked in black (discharged commercial electrolyte), red (sample groups), and blue (randomised samples).

Figure 4 displays the viscosity of the posolyte (left) and negolyte (right) as a function of SoC for  $c_{\rm V} = (1.830, 1.220)$  M and  $c_{\rm S} = 4.07$  M (top), and for  $c_{\rm S} = (4.070, 2.200)$  M and  $c_{\rm V} = 0.915$  M (bottom). The temperature is seen to have a significant impact on the viscosity of both electrolytes, specially at higher total vanadium concentrations. At  $c_{\rm V} = 0.915$  M, the viscosity behaves almost linearly with SoC. The rise in sulfates concentration also contributes to increase the viscosity, but to a lesser extend than the vanadium concentration and temperature. As a general trend, the negolyte exhibits higher viscosity and greater sensitivity to parameter variations than the posolyte.

The kinematic viscosity of each electrolyte is fitted via a third-order multivariate polynomial regression of the form

$$\nu^{j}(c_{\rm V}, c_{\rm S}, T, \text{SoC}) = \sum_{i=0}^{2} \sum_{k=0}^{2} \sum_{l=0}^{2} \sum_{m=0}^{2} \left[ F_{i,k,l,m} \left( c_{\rm V} - c_{\rm V,0} \right)^{i} \left( c_{\rm S} - c_{\rm S,0} \right)^{k} \left( T - T_{0} \right)^{l} \text{SoC}^{m} \right]$$
(3)

with the coefficients  $F_{i,k,l,m}$  being listed in Table 3. Note that the summations extend over all integral values of i, k, l, and m such that i + k + l + m < 4, hence the third-order multivariate polynomial fit. The regression for  $\nu^+$  has a root mean squared error (RMSE) of  $1.48 \cdot 10^{-2}$  mm<sup>2</sup>/s while that for  $\nu^-$  has a RMSE of  $3.16 \cdot 10^{-2}$  mm<sup>2</sup>/s. Figure 5 shows contour maps of the



Figure 3: Viscosity of the posolyte (left) and negolyte (right) versus SoC, for  $c_{\rm V} = (0.915, 1.220, 1.525, 1.830)$  M at  $T = 20^{\circ}$ C and  $c_{\rm S} = 4.07$  M. Symbols: measurements; lines: empirical regression (3).

fitted viscosity function for the posolyte (top) and the negolyte (bottom), for SoC = 0 (left), 0.5 (center), and 1 (right) at 20°C. In all cases, the viscosity is seen to increase with the total vanadium concentration, and, more weakly, with the sulfates concentration. The Supplementary Information includes two additional figures showing viscosity contours for SoC = (0, 0.5, 1) at 10°C and 30°C (Figures S2 and S3).

Just as in the previous section, the region corresponding to values of vanadium and sulfate concentrations outside the parametric range of this study is labeled as *unexplored*. Across all cases, but particularly noticeable in the negolyte, we observe a shift in trend near the boundary of this unexplored region, suggesting a reduced influence of sulfates concentration on viscosity. This trend shift is stronger as  $c_{\rm S}$  increases and as concentrations depart from the studied range. In fact, viscosity isocontours eventually reverse their direction deeper into the unexplored domain. This could simply be an artifact, as the empirical regression of  $\nu^-$  is not expected to accurately capture viscosity variations in this range due to the lack of experimental data. The posolyte viscosity  $\nu^+$  shows a similar behavior, but to a lesser extend and farther away from the studied parametric range.

## 4. Conclusion

An high-quality open-access database of density and viscosity measurements for the positive and negative electrolytes of vanadium redox flow batteries has been presented. The data contains 272 measuring points across a wide parameter space, including state of charge, total vanadium concentration, sulfate concentration, and temperature. The experimental data has been used to derive empirical regressions that provide the density of both electrolytes with a RMSE below  $10^{-3}$ g/cm<sup>3</sup>, and the viscosity with a RMSE of  $1.48 \cdot 10^{-2}$  mm<sup>2</sup>/s for the posolyte and  $3.16 \cdot 10^{-2}$  mm<sup>2</sup>/s for the negolyte.

The results reveal that the variations of density with SoC differs for the posolyte and the



Figure 4: Viscosity of the posolyte (left) and negolyte (right) versus SoC at  $T = (10, 30)^{\circ}$ C for  $c_{\rm V} = (1.220, 1.830)$  M with  $c_{\rm S} = 4.07$  M (top), and  $c_{\rm S} = (2.200, 4.070)$  M with  $c_{\rm V} = 0.915$  M (bottom). Symbols: measurements; lines: empirical regression (3).

negolyte. Thus, while the posolyte density slightly increases during charge, that of the negolyte decreases by up to 2%. Compared to density, viscosity variations are more pronounced in relative terms. They are affected by all the studied parameters, the SoC being the most relevant (without considering extreme unrealistic variations in the other parameters). This effect is amplified with higher vanadium concentrations and lower temperatures. For instance, at 10°C, a fully charged 1.83 M negolyte exhibits a viscosity that is 38% lower than when discharged.

To the best of our knowledge, this database stands out as the most extensive and highest quality available in the open literature. We attribute the quality of our data to two key factors: one the one hand, the spectrophotometric titrations used to prepare the solutions and, on the other hand, the preference for liquid weighing (whenever possible) to minimize errors associated with volume measurements. This commitment to high sample quality is reflected on the minimal statistical noise exhibited by the data points presented in section 3. We hope that these results can be of



Figure 5: Contours of  $\nu^+$  (top) and  $\nu^-$  (bottom) for the vanadium and sulphates concentration studied at 20°C and SoC = 0 (left), SoC = 0.5 (center), and SoC = 1 (right), using the empirical regression (3).

use to both the industrial and research communities, aiding to improve operational efficiency of VRFB and facilitating the development of more precise VRFB models.

#### Data availability

The raw data, containing the density and viscosity measurements, are publicly shared in the open data repository Consorcio Madroño - eCiencia Datos - UC3M [18].

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Coef.	$ u^+ $	$ u^{-}$	Unit
$F_{0,0,0,0}$	2.760	3.167	$\mathrm{mm}^2 \mathrm{s}^{-1}$
$F_{1,0,0,0}$	0.913	2.102	${\rm mm^2~s^{-1}~M^{-1}}$
$F_{0,1,0,0}$	0.483	0.413	${\rm mm^2~s^{-1}~M^{-1}}$
$F_{0,0,1,0}$	$-8.92 \cdot 10^{-2}$	-0.108	${\rm mm^2~s^{-1}~K^{-1}}$
$F_{0,0,0,1}$	-0.470	-0.898	$\mathrm{mm}^2 \mathrm{~s}^{-1}$
$F_{2,0,0,0}$	1.640	5.256	${\rm mm^2~s^{-1}~M^{-2}}$
$F_{1,1,0,0}$	0.295	-1.064	${\rm mm^2~s^{-1}~M^{-2}}$
$F_{1,0,1,0}$	$-5.89 \cdot 10^{-2}$	-0.115	${ m mm^2~s^{-1}~M^{-1}~K^{-1}}$
$F_{1,0,0,1}$	-0.161	-1.879	${\rm mm^2~s^{-1}~M^{-1}}$
$F_{0,2,0,0}$	(-)	$3.29\cdot10^{-2}$	${\rm mm^2~s^{-1}~M^{-2}}$
$F_{0,1,1,0}$	$-1.05 \cdot 10^{-2}$	$-1.02 \cdot 10^{-2}$	${\rm mm^2~s^{-1}~M^{-1}~K^{-1}}$
$F_{0,0,2,0}$	$1.54\cdot10^{-3}$	$1.96\cdot10^{-3}$	${\rm mm^2~s^{-1}~K^{-2}}$
$F_{0,0,1,1}$	$2.44 \cdot 10^{-2}$	$5.05 \cdot 10^{-2}$	${\rm mm}^2 {\rm ~s}^{-1} {\rm ~K}^{-1}$
$F_{0,0,0,2}$	0.102	0.180	$\mathrm{mm}^2~\mathrm{s}^{-1}$
$F_{2,1,0,0}$	-0.423	-1.796	${\rm mm^2~s^{-1}~M^{-3}}$
$F_{2,0,1,0}$	$-2.33 \cdot 10^{-2}$	$-4.18 \cdot 10^{-2}$	${\rm mm^2~s^{-1}~M^{-2}~K^{-1}}$
$F_{2,0,0,1}$	-0.259	-1.054	${\rm mm^2~s^{-1}~M^{-2}}$
$F_{1,2,0,0}$	0.219	0.812	${\rm mm^2~s^{-1}~M^{-3}}$
$F_{1,0,0,2}$	0.236	0.993	${\rm mm^2~s^{-1}~M^{-1}}$
$F_{0,0,1,2}$	$-5.14\cdot10^{-3}$	$-1.30 \cdot 10^{-2}$	${\rm mm}^2 {\rm \ s}^{-1} {\rm \ K}^{-1}$
$F_{1,0,2,0}$	$1.77\cdot 10^{-3}$	$2.36\cdot10^{-3}$	${ m mm^2~s^{-1}~M^{-1}~K^{-2}}$
$F_{0,0,2,1}$	$-5.04\cdot10^{-4}$	$-1.05\cdot10^{-3}$	${\rm mm^2~s^{-1}~K^{-2}}$
$F_{1,1,1,0}$	$-1.97 \cdot 10^{-2}$	$-1.21\cdot10^{-2}$	${ m mm^2~s^{-1}~M^{-2}~K^{-1}}$
$F_{1,1,0,1}$	-0.601	-0.472	${\rm mm^2~s^{-1}~M^{-2}}$
$F_{1,0,1,1}$	$3.76\cdot10^{-2}$	$7.81\cdot10^{-2}$	${ m mm^2~s^{-1}~M^{-1}~K^{-1}}$

Table 3: Coefficients for the multivariate polynomials (3) used to fit the kinematic viscosity of both electrolytes.

### **CRediT** authorship contribution statement

Pablo A. Prieto-Díaz, Ange A. Maurice: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Visualization, Project administration, Funding acquisition. Marcos Vera: Conceptualization, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

### Appendix A. Comparative analysis of density and viscosity measurements

In this section, we compare our measurements with previous data reported in the literature.

# Appendix A.1. Density

Figure A.6 shows the posolyte (left) and negolyte (right) density as a function of SoC for the three temperatures considered in the study. Our measurements (blue) correspond to  $c_{\rm V} = 1.83$  M and  $c_{\rm S} = 4.07$  M, while those reported by Skyllas et al. [3] (red) to  $c_{\rm V} = 2$  M and  $c_{\rm S} = 5$  M.



Figure A.6: Density of the posolyte (left) and negolyte (right) electrolyte versus SoC for  $T = (10, 20, 30)^{\circ}$ C, reported in this work (blue:  $c_{\rm V} = 1.83$  M and  $c_{\rm S} = 4.07$  M) and by Skyllas et al. [3] (red:  $c_{\rm V} = 2$  M and  $c_{\rm S} = 5$  M).

Despite these differences, the two datasets show very similar posolyte densities, although they differ in their response to changes in SoC. The upward trends reported by Skyllas et al. [3] exhibit an average slope of  $\rho_{SoC}^+ \simeq 8.57 \cdot 10^{-3}$  g cm<sup>-3</sup>, which is 3.2 times higher than the one reported in this work. This result supports the suggestion by Prieto et al. [12] that the value of  $\rho_{SoC}^+$  should be smaller than the one reported by Skyllas et al. in order to accommodate the recent experimental evidence on capacity fade due to imperfect electrolyte mixing in the tanks [12] with the theoretical predictions based on the value of the Richardson number [5]. However, since Skyllas et al. used significantly higher vanadium and sulfates concentrations, their posolyte densities should be larger compared to ours according to our regression fit. Regarding the negolyte, both datasets show similar variations with SoC, with a negative slope of  $\rho_{SoC}^- \simeq -2.92 \cdot 10^{-2}$  g cm<sup>-3</sup> for Skyllas et al. and  $\rho_{SoC}^- \simeq -2.64 \cdot 10^{-2}$  g cm<sup>-3</sup> from our dataset; although if we apply our fit to their vanadium and sulphates concentration it becomes even closer  $\rho_{SoC}^- \simeq -2.88 \cdot 10^{-2}$  g cm<sup>-3</sup>. This agreement is not paralleled by the density values, which exceed 2.2 % ours although such difference is still smaller than the one predicted by our fit. Regarding the effect of temperature on density, both datasets are in good quantitative agreement, with the values by Skyllas et al.,  $\rho_T^+ \simeq -5.58 \cdot 10^{-4}$  g cm<sup>-3</sup> K<sup>-1</sup> and  $\rho_T^- \simeq -6.17 \cdot 10^{-4}$  g cm<sup>-3</sup> K<sup>-1</sup>, lying just 20 % and 7 % below the ones reported here. These numbers are also in close agreement with those by Mousa [8].

The two plots in Figure A.6 do not display our regressions applied to the electrolyte composition of Skyllas et al. [3] because they fall outside our parameter range. And if they were applied, the resulting values for both electrolytes would be significantly larger. It is important to note that Skyllas et al. did not provide details about their experimental procedure nor the associated error

Coef.	Table 2	Ressel et al. [11]	Unit
$ ho_0^-$	1.3569	1.3649	${ m g~cm^{-3}}$
$ ho_T^-$	$-6.63\cdot10^{-4}$	$-6.0\cdot10^{-4}$	${\rm g}~{\rm cm}^{-3}~{\rm K}^{-1}$
$ ho_{ m SoC}^-$	$-2.30 \cdot 10^{-2}$	$-2.96 \cdot 10^{-2}$	${ m g~cm^{-3}}$

Table A.4: Multivariate regression coefficients for the density function (1) of the negolyte, as obtained from Table 2 with  $c_{\rm V} = 1.6$  M and  $c_{\rm S} = 4$  M and adapted from [11].

bars. This lack of information, coupled with the high sensitivity of  $\rho_0^j$  to vanadium and sulfates concentration (see section 3), limits our ability to further explain the discrepancies between both datasets.

Ressel et al. [11] also conducted measurements on the negolyte density for  $c_{\rm V} = 1.6$  M and  $c_{\rm S} = 4$  M, reporting a linear regression based on SoC and temperature. Our coefficients computed for their negolyte composition and their coefficients adapted to our formalism are listed in table A.4. The results are in good quantitative agreement. The value of  $\rho_0^-$  is only 0.6% higher for Ressel et al., similar to that of  $\rho_{\rm SoC}^-$ , whereas  $\rho_T^-$  is slightly lower but always in agreement with the values reported in the literature. Any discrepancies may be attributed to experimental imprecision. Ressel et al. computed the SoC using half-potentials and coulomb counting during VRFB cycling, which is less accurate than our protocol based in careful electrolyte characterisation.

#### Appendix A.2. Viscosity

Figure A.7 illustrates the dynamic viscosity of the posolyte  $\mu^+$  (top) and negolyte  $\mu^-$  (bottom) as a function of SoC at temperatures of 10°C (left), 20°C (center), and 30°C (right). Our results (blue) correspond to  $c_{\rm V} = (1.83, 1.525)$  M and  $c_{\rm S} = 4.07$  M, while those by Skyllas et al. [3] (red) correspond to  $c_{\rm V} = 2$  M and  $c_{\rm S} = 5$  M, and those by Li et al. [14] (green) to  $c_{\rm V} = (1.8, 1.6)$  M and  $c_{\rm S} = (4.5, 4.2)$  M. We plot the dynamic viscosity  $\mu^j$  instead of the kinematic viscosity  $\nu^j = \mu^j/\rho^j$ because Li et al. [14] did not report their densities, just the dynamic viscosities, thus preventing us to make the conversion. The plots also include the viscosity curves obtained from our regression fits (1)–(3) as applied to the different electrolyte compositions and temperatures.

The posolyte viscosities and their variations with the different parameters are qualitatively similar in all datasets. The viscosities reported by Skyllas et al. [3] are slightly larger than the others, as expected by their highly concentrated electrolyte. However, they are much lower than those predicted by our regressions. This effect sharpens as the predicted density was also higher. However, measurements by Li et al. [14] with  $c_{\rm V} = 1.8$  M and  $c_{\rm S} = 4.5$  M are of the same order, with a steeper decrement as SoC increases, being also lower than our regression. Their curve for  $c_{\rm V} = 1.6$  M and  $c_{\rm S} = 4.2$  M also aligns with our observed trends, showing slightly higher values compared to our measurements with  $c_{\rm V} = 1.525$  M.

Regarding the negolyte, there is a discrepancy between the solutions, but lower against our fit. Measurements by Skyllas et al. [3] and by Li et al. [14] using  $c_{\rm V} = 1.8$  M and  $c_{\rm S} = 4.5$  M have similar values and trends with SoC and temperature, but they have different electrolyte composition. The fit predicts lower viscosities for the compositions of Li et al. and higher for those of Skyllas et al. Nevertheless, measurements from Li et al. using  $c_{\rm V} = 1.6$  M and  $c_{\rm S} = 4.2$  M follow precisely our regression for the three temperatures. Note that this electrolyte composition is the one closer to our studied parametric range, so the regression is expected to provide more accurate viscosities.



Figure A.7: Dynamic viscosity of the posolyte (top) and negolyte (bottom) at  $10^{\circ}$ C (left),  $20^{\circ}$ C (center),  $30^{\circ}$ C (right) as reported in this work (blue), by Skyllas et al. [3] (red) and by Li et al. [14] (green). Dotted lines represent the predictions obtained in each case from our multivariate regressions (1)–(3).

It is important to note that Li et al. [14] utilized a Lovis 2000 M (Anton Paar) falling ball microviscometer that relies on a known density value to compute dynamic and kinematic viscosity. However, they did not specify the origin of this value, whether it was measured, computed, or obtained from the literature. This raises concerns about the accuracy of their results, as it is likely that they used the only densities available in the literature at the time, those by Skyllas et al. [3]. As previously discussed, the lack of precise information limits our ability to further explain the discrepancies between the different datasets.

# Appendix A.3. Concluding remarks

We strongly recommend our dataset for future studies because of its detailed description of experimental conditions and procedures, including well defined error estimations; the consideration of a wide range of four independent parameters; the use of precise electrolyte titration techniques for establishing the composition and state of charge of the electrolytes; and the cutting-edge equipment used for the dual measurement of density and viscosity at well controlled temperatures.

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