



# Investigation of the use of electrolyte viscosity for online state-of-charge monitoring design in vanadium redox flow battery



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## HIGHLIGHTS

- A viscosity-based online state-of-charge monitoring approach is proposed.
- Electrolyte viscosities at different SOCs and temperatures are measured.
- An empirical model that links SOC to viscosity and temperature is developed.
- The pressure drop is measured across a porous medium installed in the VFB system.
- Darcy's law is used to calculate the viscosity from measured pressure difference.

## ARTICLE INFO

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State-of-charge monitoring  
Electrolyte viscosity  
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## ABSTRACT

In vanadium redox flow batteries, an accumulated imbalance of the states-of-charge between the two half-cell electrolytes caused by vanadium ion crossover and gassing side reactions can result in only one half-cell achieving 100% state-of-charge, which is referred to as capacity loss that needs to be corrected online. In order to implement rebalancing control, online states-of-charge have to be monitored. In this paper, the electrolyte viscosity and its use for online state-of-charge monitoring design are investigated. The study firstly measures the viscosities of both  $V^{2+}/V^{3+}$  and  $VO^{2+}/VO_2^+$  redox couples in sulfuric acid as the negative and positive half-cell electrolytes at different states-of-charge and temperatures, followed by establishing an empirical neural network model that correlates the state-of-charge to viscosity and temperature. To overcome the limitation in online viscosity measurements, Darcy's law describing the flow of a fluid through a porous medium is further introduced to link the electrolyte viscosity to the pressure drop across a porous medium where the electrolyte solutions flow through. Together with the neural network model, the state-of-charge can be eventually represented as a function of pressure, temperature and flow rate that are readily measurable online, and accordingly an online state-of-charge monitoring design is developed, which could be readily integrated into the online battery control system for automated electrolyte rebalance. Experimental validation is performed on a 15-cell stack system and the results demonstrate the feasibility of the proposed method.

## 1. Introduction

With major technological advances made in renewable energy devices such as photovoltaics and wind turbine, energy storage becomes a vital issue for the integration and use of renewable energy sources in grid-scale stationary applications with the aim to compensate for the intermittent nature of solar and wind energy. Of all the existing energy storage systems, electrochemical energy storage devices are one of the most competitive candidates. Existing typical electrochemical energy storage devices include non-rechargeable primary battery, rechargeable secondary battery and rechargeable flow battery with electrolytes

stored in external reservoirs, among which flow battery has exhibited the unique and highly competitive advantages of flexibility in capacity and power output design, making it more suitable for large-scale electrical energy storage utilizations associated with solar and wind farms. Of all types of flow batteries that have reached commercial fruition, vanadium redox flow battery (VFB) invented by Skyllas-Kazacos and co-workers [1] has received the most attention and seen the greatest level of commercialization to date. The main advantage of the VFB over other flow batteries is the use of the same element in both half-cell electrolytes that fully prevents the problem of cross contamination, so the electrolytes of the VFB have a theoretically infinite life and are ease

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**Nomenclature**

$\text{VO}_2^+$ , $\text{VO}^{2+}$ , $\text{V}^{3+}$ and $\text{V}^{2+}$	vanadium redox species
$\Delta P$	pressure drop, Pa
$\mu$	dynamic viscosity of electrolyte, Pa·s
$Q$	volumetric flow rate, $\text{m}^3\text{s}^{-1}$
$L$	length of the porous medium, m
$S$	cross-sectional area of the porous medium, $\text{m}^2$

$\kappa$	permeability, $\text{m}^2$
$d_f$	fibre diameter, m
$K$	Kozeny-Carman constant
$\varepsilon$	porosity of the porous medium
$E_{\text{OCV}}$	open-circuit voltage, V
$E'_0$	formal potential, V
$R$	gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$F$	Faraday constant, $\text{C}\cdot\text{mol}^{-1}$

of maintenance. Additional benefits of the VFB include low cost for large storage capacity, minimal safety issue and high round-trip efficiency.

Despite the elimination of cross contamination between the two half-cells, however, the electrolyte solutions in a VFB have to occasionally be rebalanced due to the influence of gassing side reactions occurred at high states-of-charge (SOCs) during charging and crossover of vanadium ions of different oxidation states through the membrane that give rise to an imbalance of the states-of-charge between the two half-cell electrolytes [2]. Such an imbalance of the SOC will lead to capacity decay that limits the usable capacity over extended cycles, and this needs to be detected so that remixing or other suitable rebalancing actions can be implemented to restore the capacity of the VFB system. Therefore, online SOC monitoring methods with ease of use and good precision (< 5% error expected) are highly desirable for VFB applications over long-term operation. In practical VFB applications, the open-circuit voltage (OCV) method [3] capable of indicating the SOC of the whole cell has been widely used. In spite of ease of use and low cost, the OCV method is fairly sensitive to operation conditions (such as applied flow rate and electrolyte temperature) and more importantly unlikely to separately indicate the actual SOC of each individual half-cell as desired. To tackle this issue, several new approaches aiming to monitor each individual half-cell SOC have been introduced recently. For example, Skyllas-Kazacos et al. [4] investigated two different SOC monitoring methods for VFB control, one utilizing conductivity measurements and the other using UV-visible light absorption approaches. However, the latter cannot identify the SOC on the positive half-cell due to the excess absorbance over most of the UV-visible range. Based on the UV-visible spectra approach, Buckley et al. [5] further investigated the underlying spectroscopy of the positive electrolyte for SOC monitoring. Similarly, more accurate optical-based SOC monitoring methods were also introduced. Liu et al. [6–8] proposed to monitor the SOC by transmission spectra of the positive and negative electrolytes respectively, while Rudolph et al. [9] presented a newly developed high precision runtime measurement instrument using IR-absorption. Although these methods can achieve online detection of the SOC with high detecting resolution, a large database of the standard spectra is required for comparison with the sample spectrum and additional apparatus are also needed which adds extra cost to the VFB system. Moreover, Ngamsai et al. [10] further developed a four-pole cell device that directly realizes the measurement of the ionic resistance of the electrolyte solution. In addition, a novel ultrasonic velocity sensing approach that had been used for SOC monitoring in Li-ion and alkaline batteries was successfully demonstrated to monitor the SOC of a VFB by Chou and co-workers [11]. More recently, model-based observation methods for online SOC monitoring of the VFB were described by Xiong and Wei [12–15], which essentially use a first-order resistor capacitor model to model flow battery dynamics such as activation and concentration polarizations. This method is favorable for incorporating into the battery management system, but compared with chemical property based methods the electrical circuit model commonly used for secondary batteries tends to be inadequate in capturing flow battery dynamics that are closely associated with the changes of redox species in the electrolyte, due to the fact that the variation in electrolyte flow during operation can significantly influence the cell polarizations which

cannot be modelled by the simple resistor capacitor model.

Although all the approaches mentioned above provide a solution to online SOC detection that may be suitable for use in VFB systems depending on specific requirements of the application, it is found in practice that they either require additional equipment that increases the system cost or become less accurate and even impractical to set up when applying to complex large-scale VFB application systems. Therefore, developing an online SOC monitoring method with low cost, robust to operating conditions and flexibility in monitoring each individual half-cell SOC is urgent for use in practical large-scale VFB systems. Similar to electrolyte conductivity, the electrolyte viscosity is also a measurable physical property of electrolyte with its value varying with the electrolyte composition and concentration [16]. Motivated by this feature, the SOC of each half-cell electrolyte can be readily linked to its viscosity, making it possible to develop methods for online state-of-charge monitoring. Although online measurement of the electrolyte viscosity is still impractical for most of the chemical applications including flow batteries, the inherent nature of viscosity of a fluid that closely associates with shear stress offers an alternative solution to real-time viscosity calculation by using the measured pressure difference across a porous medium where the electrolyte flows through in accordance with Darcy's law. Luckily, the pressure transducers have already been widely employed in most of the commercial VFB systems for monitoring and indication of any abnormal conditions in the stack arising from blockage and electrolyte leakage, which allows the pressure difference across a porous medium to be readily measured online. Hence, such a viscosity-based online SOC monitoring technique is viable and of great convenience for VFB applications.

In this paper, the electrolyte viscosity and its use for VFB online state-of-charge monitoring design are for the first time investigated. The study firstly measures the viscosities of both positive and negative half-cell electrolytes at different SOC and temperatures for two compositions of vanadium solutions in Section 3.1, followed by establishing an empirical neural network model that relates the SOC to the electrolyte viscosity and temperature in Section 3.2. To overcome the limitation in online viscosity measurements, Darcy's law is further introduced in Section 3.3 to link the electrolyte viscosity to the pressure drop across a porous medium where the electrolyte solutions flow through, which, along with neural network model, finally establishes a desired relationship between the SOC of the electrolyte and the pressure, temperature and flow rate that are readily measured online. Based on these, an online state-of-charge monitoring approach is described in Section 3.4, which neither brings in any expensive measuring equipment nor introduces additional complicated sensors, while taking the advantage of the use of pressure and temperature transducers as well as flow meters that are commonly applied in most of the commercial VFB systems. Experimental validation was performed on a 15-cell stack VFB system in Section 3.5 and the results have demonstrated the feasibility of the proposed method. Such a viscosity-based SOC monitoring design and approach could be readily integrated into the online advanced battery control system that realizes automated electrolyte rebalance.

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