

Redox flow battery time-varying parameter estimation based on high-order sliding mode differentiators

Pedro Fornaro*¹ | Thomas Puleston² | Paul Puleston¹ | Maria Serra-Prat² | Ramon Costa-Castelló² | Pedro Battaiotto¹

¹Instituto LEICI, Universidad Nacional de la Plata - CONICET, Departamento de Electrotécnica, 48 y 116 s/n, La Plata (1900), Buenos Aires, Argentina

²Institut de Robòtica i Informàtica Industrial, CSIC-UPC, Llorens i Artigas 4-6, 08028 Barcelona, España

Correspondence

*Email: pedro.fornaro@ing.unlp.edu.ar
Email: tpuleston@iri.upc.edu
Email: puleston@ing.unlp.edu.ar
Email: maria.serra@upc.edu
Email: ramon.costa@upc.edu
Email: pedro@ing.unlp.edu.ar

Abstract

A new insight into vanadium redox flow batteries (VRFB) parameter estimation is presented. Driven by the electric vehicles proliferation, a hybrid fast charging station with grid and renewable energy connection is particularly considered. In this stationary application, the VRFB is operating as buffering module. This hybrid topology could contribute to reduce the grid connection cost of the charging station. However, to make VRFB a viable technology, improvements are needed. Among these, some of the most important are in the field of the estimation of the battery's State of Charge, State of Health, and internal parameters.

The proposed estimation method is based on a recursive least square (RLS) estimation algorithm with forgetting factor, combined with a sliding mode finite-time convergent differentiation algorithm. The latter provides robust exact derivatives of both VRFB's current and voltage with a high degree of noise rejection, required by the RLS algorithm to perform a precise estimation. The proposed sliding mode based estimation setup is completed with a systematic methodology to guarantee the validity of the on-line estimated values, depending on the persistence of excitation of the measured current and voltage. Finally, the methodology is thoroughly analysed and validated by computer simulation.

KEYWORDS:

Vanadium redox flow battery, parameter estimation, State of Charge, State of Health, sliding mode differentiator.

1 | INTRODUCTION

Throughout the last two centuries, economic and industrial development has relied on the massive exploitation of fossil fuels as an energy source. However, in the course of the 21st century, renewable energies have experienced a significant growth which

is expected to intensify during the next decades. According to a 2020 European Commission Report [1], it is expected that by 2050 at least 50% of the energy produced in Europe will come from renewable sources, while other global organisations such as the International Energy Agency have set even more ambitious goals. The tremendous interest in the development of renewable energies is motivated on the one hand by the growing demand for energy and the depletion of traditional non-renewable energy sources and, on the other hand, by the need to limit and, ultimately, reverse the serious environmental damage associated with the use of fossil fuels. In addition, renewables are of particular strategic interest to those countries that lack significant reserves of fossil fuels and are dependent on energy imports [2].

This transition towards a new sustainable matrix based on renewable energies of unpredictable and intermittent nature (solar, wind, marine, etc.) brings with it a set of challenges. One of them is the development of versatile energy storage systems (ESS), capable to complement the renewables, storing the energy surplus and, timely, delivering when required [3]. Moreover, those ESS technologies open new innovation fields, such as more efficient smart microgrids, for off-grid supply, or hybrid energy applications, for systems weakly connected to the grid [4].

Among ESS, redox flow batteries (RFB) are one of the technologies that are receiving a great deal of attention for large-scale energy storage in stationary applications [5][6]. Regarding the most important features of RFB it can be mentioned their high efficiency (~80%), simple and safe operation, rapid response time, independence between power output and capacity, long service life and suitability for long term storage with very little self discharge [7]. In addition, they require low maintenance and, if necessary, can be quickly refuelled by renewing the tanks content [8]. Among the different types of RFB developed so far, all-vanadium redox flow batteries (VRFB) are the most studied and developed so that they are generally considered the closest to reach a commercial breakthrough [9]. The main benefit of this technology is that, as vanadium is the active specie in both half-cells, degradation problems related to the cross-contamination of the electrolytes are eliminated [3][10].

The aforementioned features make VRFB an excellent option to be used in combination with renewable energies, as a key part in the peak shaving and load levelling processes [11]. Additionally, VRFB may be used as a backup power in those facilities in which it is crucial to guarantee a continuous supply even if the main power fails [7]. There are also ongoing efforts to achieve higher energy densities that would make RFB suitable to power electric vehicles [12].

One specific application in which VRFB could perform particularly well is as a buffering stationary ESS in electric vehicles (EV) charging stations [13]. The rapid growth in the proportion of EV, in combination with the development of new fast charging technologies of over 100 kW, may give rise to issues, such as grid stability problems and costly transformers and ancillaries, required for interconnection with the charging station.

However, it has been found that the demand curve heavily varies throughout the day and the peak power is only reached in relatively short periods. In this context, a proposed solution to deal with this problem is to use a suitable ESS, such as redox flow batteries, to gradually store energy during low-demand periods, to be released during load peaks [14]. Therefore, this hybrid

topology would contribute to reduce the grid connection cost of the EV charging station and, additionally, during low demand it could be used to improve the grid power quality.

In spite of VRFB's auspicious prospect, some issues of this technology have yet to be adequately addressed in order to make them viable for widespread use. One of the most important problems that needs to be solved is the estimation of the battery parameters, being the State of Charge (SoC) and the State of Health (SoH) two of the most relevant [6][15]. It is a fact that at the laboratory level there are analytical techniques to determine the SoC, such as spectrophotometric studies [16] or electrolyte conductivity [17]. However, to implement them in actual applications, expensive instrumentation is required that would significantly increase the cost and complexity of the facilities. An alternative approach to determine the fundamental parameters of the RFB is to develop efficient estimation systems relying on easily measurable variables, such as the cells' terminal voltages and current [18][19].

To estimate the SoC and SoH of a variety of ESS, different topologies based on sliding mode (SM) techniques have been proposed (e.g. [20][21][22]) to take advantage of the inherent versatility and robustness of this non-linear approach [23][24]. Amongst the most successful are the adaptive SM based observers (SMO), which include a parameters' estimation setup to provide the observer updated parameters of the system. However, there exists a trade-off between the utilisation of high gains, to improve the convergence speed, and the worsening of the so-called chattering effect together with an increase in sensitivity to noises [25][26]. Also, in high order SMO the stability and convergence of this approach is not always easy to establish [27].

Resourceful alternative solutions were developed resorting to estimation setups based on the use of SM Differentiators (SMD) [28][29][30]. Some implementation difficulties regarding their noise sensitivity and required sampling time originally existed, however novel high order SMD, such as the filtering differentiators (SMFD), have shown considerable improvements in that area [31]. They provide finite-time convergence up to the n -th time derivative of a $(n+1)$ -Lipstchizian signal. Consequently, by describing the system in the generalised Fliess canonical form, the separation principle applies and it is possible to separately and robustly estimate the ESS parameters and states, as introduced by the authors in [32].

On the basis of the above mentioned ideas, an on-line estimation methodology for a VRFB employed as a stationary ESS is developed in this paper. Specifically, the VRFB is operating as buffering module of a hybrid EV charging station [13], with grid and renewable energy connection (as presented in Figure 1).

By combining a Recursive Least Square (RLS) estimation algorithm with forgetting factor and the SMFD, the proposed method is capable to obtain the time-varying parameters of a VRFB's equivalent electric circuit model (ECM), improving the estimation results by means of a high degree of noise rejection, a reduced chattering and faster convergence rate. The SMFD provides, in finite time, robust exact derivatives of both current and voltage of the VRFB, required by the RLS algorithm to perform a precise estimation. The proposed SMFD-based estimation setup is completed with a systematic methodology to ensure

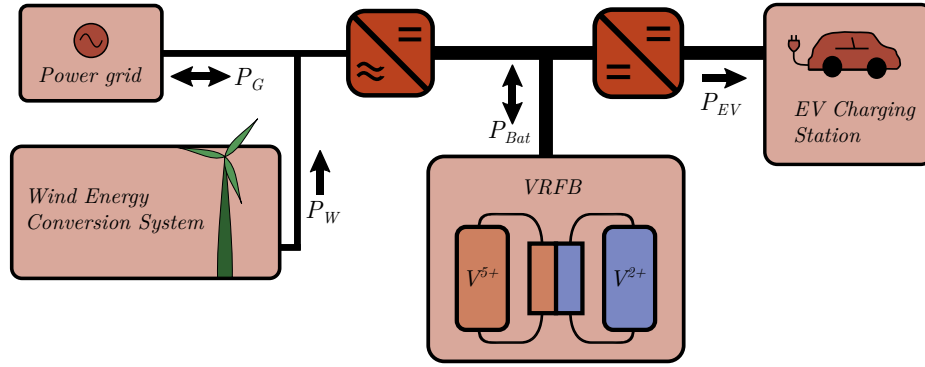


FIGURE 1 Schematic of the hybrid EV charging station with VRFB as buffer.

the validity of the on-line estimated values, depending on the persistence of excitation [32] (i.e., the frequency content richness) of the VRFB current and voltage.

2 | VANADIUM REDOX FLOW BATTERY MODELLING

There exist several model approaches to characterise the VRFB depending on the level of detail required and on the targeted objective. They can be primarily classified as distributed parameter models (DPM), if they consider a spatial distribution of the system variables and parameters (see e.g. [10][33]), or as lumped parameter models (LPM), if they concentrate all the information of the system into a set of discrete entities with uniform properties [3][34][35].

The former are the most accurate, and can constitute powerful tools for certain fields of R+D, but at the expense of complex and cumbersome handling. On the other hand, LPM are mathematically much simpler and are successfully used for the design of control and observation strategies. In particular, equivalent electric circuit models (ECM) are a widely used type of LPM. Although they present some limitations to precisely reflect the details of the physic and chemical processes involved, they demonstrate excellent adaptability and a great deal of accuracy in predicting the electric dynamic response [36][37][38]. Specifically, time-varying ECMs improve the modelling accuracy over their time-invariant counterparts. Thanks to these features and their relative simplicity, together with fast computational time, they have proved to be well suited for on-line estimation applications [19][26][39].

In the remainder of this section, a brief description of the VRFB operation is introduced and its ECM and fundamental dynamic equations are presented.

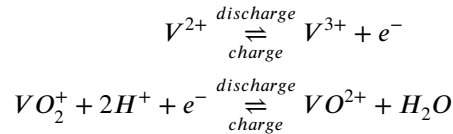
2.1 | Fundamentals of a Vanadium Redox Flow Battery

In VRFB, electrical energy is obtained from the electron transfer redox reaction between vanadium species with different oxidation states. Vanadium ions are dissolved in sulphuric acid solutions, which are stored in two independent reservoirs. The negative

electrolyte contains V^{2+} and V^{3+} , while the positive one contains V^{4+} and V^{5+} (the latter in the form of the oxides VO^{2+} and VO_2^+ , respectively) [34].

When the battery is operating, the electrolytes contained in the tanks are pumped through a stack of cells, where the chemical reaction takes place. Inside the stack, both solutions are kept separated by a proton exchange membrane, which allows to keep the electrical neutrality of the solutions during the processes of charge and discharge. Since the fluids go through a closed circuit, once they leave the stack, they are returned to their respective tanks.

The reactions that take place at the surface of the electrodes of the cells are the following:



The concentration in the tanks of the vanadium “charged species” (V^{2+} and V^{5+}) is directly related to the energy stored in the system. Evidently, charged species concentrations will increase during charge operation and decrease during discharge. Normally, VRFB are balanced, i.e., the fluid volume in both tanks is the same and the concentrations of V^{2+} and V^{3+} in the negative electrolyte are equal to the concentrations of V^{5+} and V^{4+} in the positive electrolyte, respectively.

As a consequence of the previous analysis, the SoC, typically defined as the ratio of the charge stored in the battery (Q) and its total capacity (Q_M), can also be expressed as the quotient between the concentration of the active species and the total concentration of vanadium [37][38].

$$SoC = \frac{Q}{Q_M} = \frac{c_2}{c_2 + c_3} = \frac{c_5}{c_4 + c_5} \quad (1)$$

with c_2 , c_3 , c_4 and c_5 , the vanadium species concentrations.

The equilibrium voltage generated by the chemical reaction at open circuit, can be calculated by means of the Nernst equation [38]:

$$v_{oc}^{cell} = E^0 + \frac{RT}{F} \ln \left[\left(\frac{c_2 c_5 c_H^2}{c_3 c_4} \right) \left(\frac{\gamma_2 \gamma_5 \gamma_H^2}{\gamma_3 \gamma_4} \right) \right] \quad (2)$$

where E^0 is the standard cell voltage, F is the Faraday constant, c_H is the H^+ concentration and γ_i are the activity coefficients of the species involved in the reaction.

In practice, Eq. (2) can be reduced assuming that the activity coefficients and c_H remain approximately constant throughout operation [34][38]. Then, E^0 can be replaced by a nominal voltage (E^θ) that groups all the constant terms in Eq. (2) whose value is approximately 1.35V and represents the v_{oc}^{cell} when SoC=50%. Under these assumptions, and substituting Eq. (1) in Eq. (2), a simplified expression for the Nernst equation is obtained:

$$v_{oc}^{cell} = E^\theta + \frac{2RT}{F} \ln \left(\frac{SoC}{1 - SoC} \right) \quad (3)$$

Eq. (3) provides a sufficiently accurate description of the open-circuit voltage within a maximum and minimum SoC, SoC_{min} and SoC_{max} respectively, that fully covers an extended operating range of the battery. Typically, VRFB operate between SOC limits of 10% and 90%, that correspond to a v_{oc}^{cell} of 1.24V and 1.46V, respectively.

In applications that require stacks of N cells in series, the open-circuit voltage of the stack is straightforwardly given by:

$$v_{oc} = N v_{oc}^{cell} = N \left[E^\theta + \frac{2RT}{zF} \ln \left(\frac{SoC}{1 - SoC} \right) \right] \quad (4)$$

2.2 | Equivalent electric circuit model of the vanadium redox flow battery

The electrical equivalent circuit used in this paper to represent the VRFB, is displayed in Figure 2. Note that all the parameters are assumed to be time-varying, with a slow rate of variation with respect to the estimation algorithm computation time.

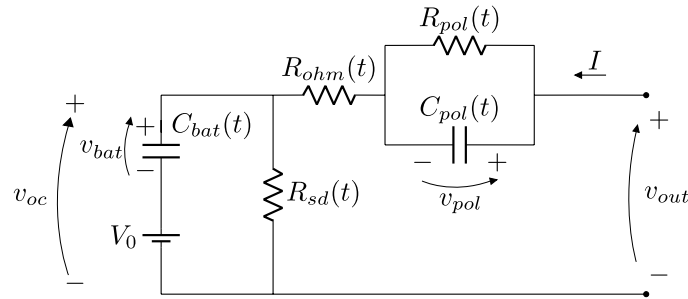


FIGURE 2 Equivalent electric circuit model of the VRFB.

The $v_{oc} = v_{bat} + V_0$ is modelled with the series of a constant source, that corresponds to the minimum open-circuit voltage ($V_0 = v_{oc}(SoC_{min})$) and a capacitor C_{bat} , whose electrical charge accounts for the available charge stored in the VRFB. The capacitor varies in accordance with the non linear function $\partial Q / \partial v_{oc}$, defined by the Nernst equation (Eq. (4)). Consequently, it varies over time as the battery is charged and discharged and it is modelled with a time-varying capacitor $C_{bat}(t)$.

The series resistance R_{ohm} stands for the ohmic losses due to the resistance of the porous electrodes, electrolyte, membrane and bipolar plates [40][41]. As for the parallel $R_{pol}C_{pol}$ network, it represents transient dynamics, such as activation and concentration polarisation [19][37][38][39].

Finally, a parallel resistance R_{sd} is included to model the self-discharge of the VRFB. The reasons of this phenomenon are twofold. On the one hand, the shunt currents caused by a potential gradient between cells. On the other, undesired diffusion of vanadium ions through the membrane [37]. Note that during normal healthy operation of the VRFB, the incorporation of R_{sd} may just incrementally improve the model's accuracy, due to its (typically) high value. However, taking into account the self-discharge phenomenon in the model is of special interest for the proposed method, allowing to detect possible malfunctions, such as membrane degradation or electrolyte leak.

2.3 | Dynamic equations and Fliess Canonical Form

The linear time-varying description of the VRFB is given by:

$$\left\{ \begin{array}{l} \underbrace{\begin{bmatrix} \dot{v}_{oc} \\ \dot{v}_{pol} \end{bmatrix}}_{\dot{\mathbf{x}}} = \underbrace{\begin{bmatrix} \frac{-1}{R_{sd}C_{bat}} & 0 \\ 0 & \frac{-1}{R_{pol}C_{pol}} \end{bmatrix}}_{\mathbf{A}} \underbrace{\begin{bmatrix} v_{oc} \\ v_{pol} \end{bmatrix}}_{\mathbf{x}} + \underbrace{\begin{bmatrix} \frac{1}{C_{bat}} \\ \frac{1}{C_{pol}} \end{bmatrix}}_{\mathbf{B}} I \end{array} \right. \quad (5a)$$

$$\left\{ \begin{array}{l} v_{out} = \underbrace{\begin{bmatrix} 1 & 1 \end{bmatrix}}_{\mathbf{C}} \underbrace{\begin{bmatrix} v_{oc} \\ v_{pol} \end{bmatrix}}_{\mathbf{x}} + \underbrace{\begin{bmatrix} R_{ohm} \end{bmatrix}}_{\mathbf{D}} I \end{array} \right. \quad (5b)$$

where the state variables $\begin{bmatrix} v_{oc} & v_{pol} \end{bmatrix}^T$ are the open-circuit voltage and the C_{pol} voltage. I and v_{out} are the current and the output voltage of the VRFB, respectively. The argument t in the parameters has been omitted for the sake of conciseness.

For the estimation method the system must be transformed into the generalised Fliess canonical form, obtained by defining the transformed states $\mathbf{z}$ as the system's output and its consecutive time derivatives, i.e. $z_1 = v_{out}$, $z_2 = \dot{z}_1 = \dot{v}_{out}$. Accordingly, the transformation diffeomorphism is defined as:

$$\mathbf{z} = \Phi(\mathbf{x}, I, \dot{I}) = \begin{bmatrix} z_1 \\ z_2 \end{bmatrix} = \begin{bmatrix} \mathbf{C} \\ \mathbf{CA} \end{bmatrix} \begin{bmatrix} v_{oc} \\ v_{pol} \end{bmatrix} + \begin{bmatrix} \mathbf{D} \\ \mathbf{CB} \end{bmatrix} I + \begin{bmatrix} \mathbf{0} \\ \mathbf{D} \end{bmatrix} \dot{I} \quad (6)$$

and the linear time-varying system described in Fliess canonical form results:

$$\begin{cases} \dot{z}_1 = z_2 & (7a) \\ \dot{z}_2 = m_1 \ddot{I} + m_2 \dot{I} + m_3 I + m_4 z_2 + m_5 z_1 & (7b) \\ y = z_1 & (7c) \end{cases}$$

where m_1 to m_5 are algebraic combinations of the ECM resistances and capacitances. Assuming that the electric elements of the ECM are slowly time varying for almost all t then:

$$m_1 = R_{ohm} \quad (8a)$$

$$m_2 = \frac{1}{C_{bat}} + \frac{1}{C_{pol}} + R_{ohm} \left(\frac{1}{C_{pol} R_{pol}} + \frac{1}{C_{bat} R_{sd}} \right) \quad (8b)$$

$$m_3 = \frac{R_{sd} + R_{pol} + R_{ohm}}{C_{bat} R_{sd} \cdot C_{pol} R_{pol}} \quad (8c)$$

$$m_4 = -\frac{C_{bat} R_{sd} + C_{pol} R_{pol}}{C_{bat} R_{sd} \cdot C_{pol} R_{pol}} \quad (8d)$$

$$m_5 = -\frac{1}{C_{bat} R_{sd} \cdot C_{pol} R_{pol}} \quad (8e)$$

Observe that Eq. (7b) is linear in the unknown parameters m_1 to m_5 , and therefore it is possible to perform a linear regression to obtain the ECM time-varying parameters, as described in the following section.

3 | VRFB ON-LINE ESTIMATOR BASED ON SLIDING MODE FILTERING DIFFERENTIATION

The proposed methodology for on-line estimation of VRFB is laid out in this section. This proposal is capable to provide in a prescribed fixed time, with robust noise rejection and known error upper bound, the parameters of the VRFB. To achieve this, a recursive least squares (RLS) with forgetting factor algorithm in combination with a SMFD algorithm is employed. To the interested reader, further details about RLS-SMFD estimation can be found in [32].

The primal groundwork introduced in [32] was intended for an electric vehicle application with Li-ion battery/Supercapacitor. Therefore, diverse aspects need to be considered and several modifications are required to develop a novel methodology capable to deal with a VRFB stationary energy storage application. Firstly, due to the inherent differences between the nature and constitution of the former ESSs and these flowing electrolyte batteries. And secondly, but not least important, because of the power regime in VRFB stationary applications, where the existence of periods of steady current is not infrequent.

Effectively, in many VRFB applications, particularly in EV charging stations, the current demand intermittently lacks of enough persistence of excitation (PE). In the case under study, for instance, this may happen during intervals with low contribution from the wind energy conversion system. Then, to conduct the estimation with favourable PE conditions, the proposed methodology contemplates, if required, the injection of an appropriate persistent signal to the VRFB current profile (based on, for instance, multisine or filtered PRBS signals).

In addition, the VRFB parameter estimation methodology incorporates a simultaneous dual estimation setup. A 4th-order reduced estimation is run, to rapidly estimate the parameters, during VRFB healthy operation when the self-discharge resistance

R_{sd} is high, hence negligible. In parallel, a 5th-order complete estimation is conducted at a lower rate, to monitor the SoH by detecting if the self-discharge losses reach a critical inadmissible value.

3.1 | Dual on-line parameter estimation algorithm

In this subsection the RLS with forgetting factor algorithm is presented. It is constructed assuming that robust estimations for the first and second order derivatives of both current and voltage of the VRFB are available (this issue will be addressed in Subsection 3.3).

- *4th-order reduced estimation regression equation*

During normal functioning, particularly when the VRFB's membrane is healthy, the value of the self-discharge resistance R_{sd} is high, thus its effect in the ECM (Figure 2) is negligible. Therefore, in practice, the implementation of a more convenient faster reduced-order estimator is recommended, to obtain the significant elements C_{bat} , R_{ohm} , C_{pol} and R_{pol} .

Considering that under normal operation $R_{sd} \gg R_{ohm} + R_{pol}$ and $C_{bat} R_{sd} \gg C_{pol} R_{pol}$ hold, parameters m_2 to m_4 can be straightforwardly reduced and, more importantly, parameter m_5 can be neglected.

Consequently, from Eq. (7b) the reduced-order regression equation is obtained:

$$\begin{aligned} \eta(t) = \dot{z}_2 = \ddot{y} &= \boldsymbol{\theta}_4(t)^T \boldsymbol{\varphi}_4(t) = \\ &= \begin{bmatrix} m_1 & m_2 & m_3 & m_4 \end{bmatrix} \begin{bmatrix} \ddot{I} & \dot{I} & I & z_2 \end{bmatrix}^T \end{aligned} \quad (9)$$

where $\boldsymbol{\varphi}_4(t) \in \mathbb{R}^4$ is the linear regressor and $\boldsymbol{\theta}_4 \in \mathbb{R}^4$ is the unknown ECM parameters vector.

- *5th-order complete estimation regression equation*

As previously stated, a five-parameter estimation results in detriment of the convergence estimation time bound. However, this slower estimation is still very useful to monitor the SoH of the exchange membrane, by checking the evolution of parameter R_{sd} (as will be shown in Subsection 4.2).

Then, the 5th-order estimation regression equation is directly given by Eq. (7b):

$$\begin{aligned} \eta(t) = \dot{z}_2 = \ddot{y} &= \boldsymbol{\theta}_5(t)^T \boldsymbol{\varphi}_5(t) = \\ &= \begin{bmatrix} m_1 & m_2 & m_3 & m_4 & m_5 \end{bmatrix} \begin{bmatrix} \ddot{I} & \dot{I} & I & z_2 & z_1 \end{bmatrix}^T \end{aligned} \quad (10)$$

where $\boldsymbol{\varphi}_5(t) \in \mathbb{R}^5$ is the full-order linear regressor and vector $\boldsymbol{\theta}_5 \in \mathbb{R}^5$ contains the complete unknown parameters presented in Eq. (8).

To conduct both estimations (employing either Eq. (9) or Eq. (10)) a similar procedure is followed. A recursive expression to obtain the ECM parameters estimates, $\hat{\theta}(t)$, is proposed as in [32]:

$$\dot{\hat{\theta}}(t) = -\mathbf{G} [\mathbf{R}(t)\hat{\theta}(t) + \mathbf{r}(t)] \quad (11a)$$

$$\dot{\mathbf{R}}(t) = -q\mathbf{R}(t) + \boldsymbol{\varphi}(t)\boldsymbol{\varphi}^T(t) \quad (11b)$$

$$\dot{\mathbf{r}}(t) = -q\mathbf{r}(t) - \boldsymbol{\varphi}(t)\eta(t) \quad (11c)$$

where vector $\mathbf{r}(t)$ and positive semi-definite matrix $\mathbf{R}(t)$ are auxiliary variables, initialised in zero: $\mathbf{r}(t_0) = \mathbf{0} \in \mathbb{R}^k$, and $\mathbf{R}(t_0) = \mathbf{0} \in \mathbb{R}^k$ with $k = 4, 5$ as applicable. The gain matrix $\mathbf{G}$ and the forgetting factor q are design parameters, such that:

- The forgetting factor q exponentially weights with a time constant $\tau = 1/q$ the measured data used in the estimation.
- $\mathbf{G}$ is a symmetric positive definite gain matrix, designed to determine the algorithm convergence rate, which depends directly on its minimum eigenvalue ($\lambda_{\min}(\mathbf{G})$).

For the estimation algorithm to work, it is required the input signals to posses sufficient persistence of excitation. In this proposal, such PE condition is verified on-line by computing the minimum eigenvalue of $\mathbf{R}(t)$, $\lambda_{\min}(\mathbf{R}(t))$. Effectively, it has been proved in [32] that if $\lambda_{\min}(\mathbf{R}(t))$ is large enough (i.e, if it exceeds an appropriate threshold), then the excitation is sufficiently persistent to ensure estimation convergence in a desired time.

Specifically, with an adequate selection of parameters q and $\mathbf{G}$, an exponential upper bound for the error convergence time t_e is T_e :

$$\begin{aligned} t_e &\leq \frac{n_\tau}{2 \cdot \lambda_{\min}(\mathbf{G}) \cdot \lambda_{\min}(\mathbf{R}(t))} \leq \\ &\leq \frac{n_\tau}{2 \cdot \lambda_{\min}(\mathbf{G}) \cdot \lambda_{Th}} = T_e \end{aligned} \quad (12)$$

with $\lambda_{Th} > 0$ and $n_\tau > 0$ as design constants. λ_{Th} is the threshold in the so called *Estimation Condition*:

$$\lambda_{\min}(\mathbf{R}(t)) \geq \lambda_{Th} \quad (13)$$

When Eq. (13) holds, the parameters convergence is ensured in a prescribed T_e . The threshold λ_{Th} is set empirically in accordance with the PE of the characteristic power demand profile of each type of application.

For its part, the design value n_τ is the number of time constants of the exponential convergence bound Eq. (12), therefore it determines the estimation accuracy. For instance, selecting $n_\tau = 2.5$ ensures that, at least, a 91% accuracy in the parameter estimation can be achieved within time T_e .

3.2 | Estimation methodology based on persistence of excitation analysis

The proposed estimation methodology, designed to guarantee the estimation accuracy in a prescribed convergence time T_e , comprises the following steps (an associated flow chart can be seen in Fig. 3):

1. *FSMD Initialisation.*

The estimation is initially disabled, by zeroing the gain matrix $\mathbf{G}$ in Eq. (11a). In parallel, a finite time differentiation process based on SMFD is triggered (see details in 3.3). Once the SMFD algorithms converge, robust computations for the VRFB voltage, current, and its derivatives are available to proceed with the estimation process.

2. *Persistence of Excitation Checking.*

To evaluate the PE on-line, $\lambda_{\min}(\mathbf{R}(t))$ is continuously computed, by solving Eq. (11b). Simultaneously, a timer starts to count the *Inactive Estimation Time* (T_i). For a given application, a maximum admissible T_{iMax} is set (e.g., for the VRFB under study $T_{iMax} = 200s$).

3. *Estimation Pause.* When the estimation enters in this step, the matrix $\mathbf{G}$ is set equal to zero ($\mathbf{G} = 0$). Additionally, a *Triggering Condition* is defined as $\lambda_{\min}(\mathbf{R}(t)) \geq k\lambda_{Th}$, ($k > 1$). If the *Triggering Condition* is satisfied, then proceed to *Step 4*. Else, the process continues in the *Step 3*, if $T_i < T_{iMax}$, or goes forward to *Step 5*, if the maximum *Inactive Estimation Time* is reached, i.e., $T_i \geq T_{iMax}$. Remark: with $\mathbf{G} = 0$, the estimates are held constant.

4. *Estimation Active.*

The estimation process is enabled by restoring the gain matrix $\mathbf{G}$ to its designed value (and the *Inactive Estimation Time* T_i is set equal to zero). The estimation process continues as long as the *Estimation Condition* $\lambda_{\min}(\mathbf{R}(t)) \geq \lambda_{Th}$ holds. Else, i.e., $\lambda_{\min}(\mathbf{R}(t))$ falls below λ_{Th} , the estimation must be paused, so it goes back to *Step 3*.

5. *Small-magnitude persistent signal injection.*

To avoid inadmissible long periods ($T_i > T_{iMax}$) without valid estimates due to lack of PE, a small-magnitude persistent signal is added to the VRFB current demand profile, sufficient to fulfil the *Triggering Condition*. Then, the process goes back to *Step 4*. Note that the persistently exciting signal should be injected over a time $T_{injection}$ longer than T_e , in accordance with the prescribed convergence time (a suggested value is $T_{injection} = T_e + 1/q$).

3.3 | Sliding mode based differentiation algorithm

The success of the proposed estimation methodology heavily relies on the accuracy of the first and second time derivatives of both current and voltage of the VRFB, that conform the linear regressor $\boldsymbol{\varphi}(t)$ required in the computation of Eq. (11). Therefore,

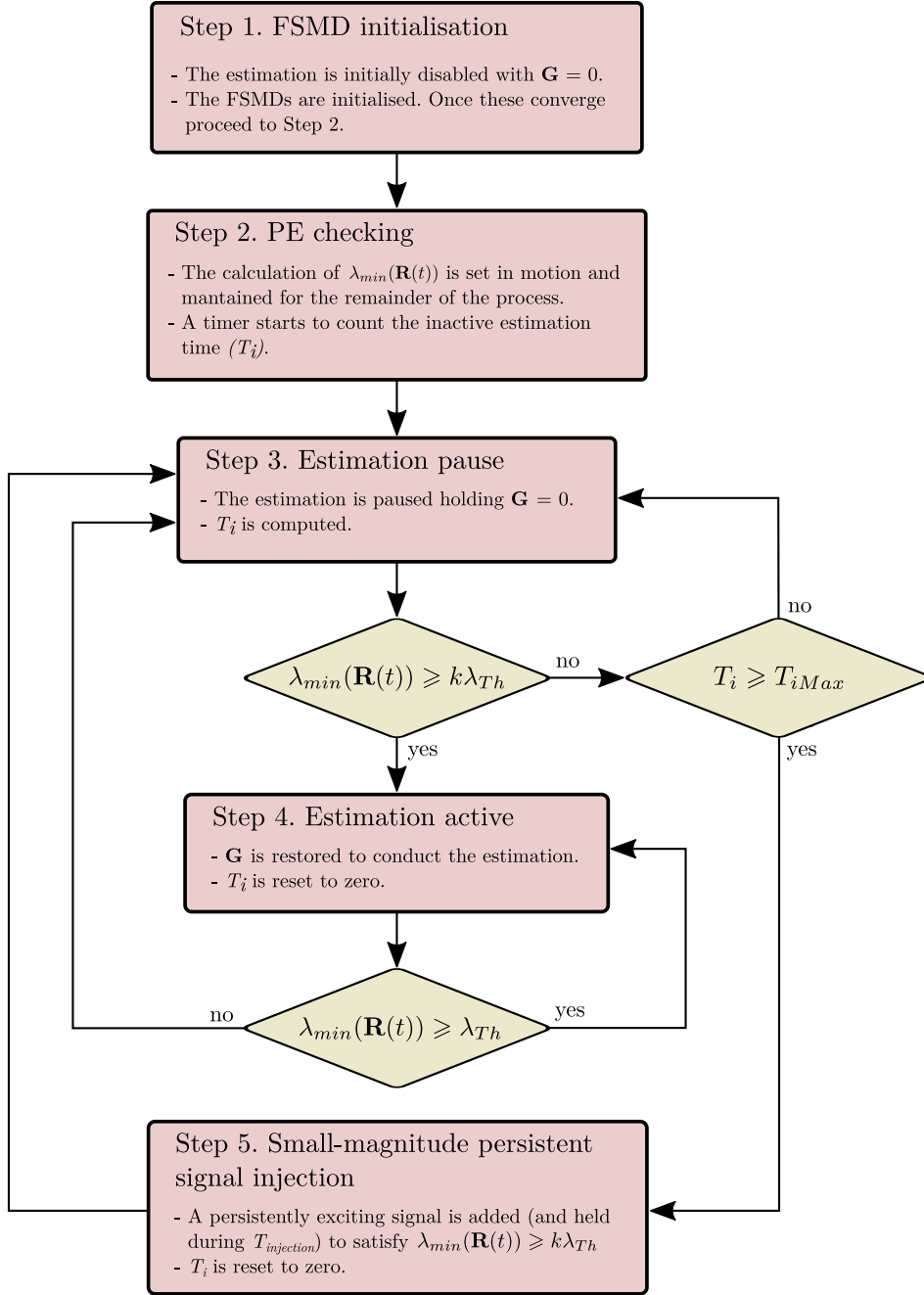


FIGURE 3 Estimation methodology flow chart.

a centrepiece of the proposal is the design of an advanced differentiation algorithm, equipped to compute robust exact derivatives of such VRFB electric variables in the presence of noise.

To this end, a SMFD [31] is incorporated in the estimation setup. In general terms, these differentiators are capable to provide in finite time up to the n_{th} time derivative of an unknown input signal provided the following conditions [31]:

- With positive $\varepsilon_{1,2}$, the noise η contained in the signal to differentiate is locally bounded, i.e. $|\epsilon| \leq \varepsilon_1$, or possibly unbounded with a small local average value e.g. $\int |\epsilon| dt \leq \varepsilon_2$.

- There exists a known Lipschitz constant $L > 0$ for the n_{th} time derivative of the signal to differentiate.

Then, the SMFD structure to compute in finite time the first and second time derivatives of a given signal $f(t)$ is:

$$\dot{w}_1 = -\lambda_4 L^{1/5} |w_1|^{4/5} \text{sign}(w_1) + w_2 \quad (14a)$$

$$\dot{w}_2 = -\lambda_3 L^{2/5} |w_1|^{3/5} \text{sign}(w_1) + (\mu_1 - f(t)) \quad (14b)$$

$$\dot{\mu}_1 = -\lambda_2 L^{3/5} |w_1|^{2/5} \text{sign}(w_1) + \mu_2 \quad (14c)$$

$$\dot{\mu}_2 = -\lambda_1 L^{4/5} |w_1|^{1/5} \text{sign}(w_1) + \mu_3 \quad (14d)$$

$$\dot{\mu}_3 = -\lambda_0 L \text{sign}(w_1) \quad (14e)$$

The outputs of the SMDF are μ_1 , μ_2 and μ_3 , which tend to the input signal and its derivatives, respectively (i.e., $\mu_1 \rightarrow f(t)$, $\mu_2 \rightarrow \dot{f}(t)$ and $\mu_3 \rightarrow \ddot{f}(t)$). While w_1 and w_2 are auxiliary variables, and the constants λ_0 to λ_4 are design parameters, empirically adjusted to guarantee the algorithms convergence within a small error bound [30]. Following these recommendations the gains are set as: $\lambda_0 = 1.1$, $\lambda_1 = 4.57$, $\lambda_2 = 9.3$, $\lambda_3 = 10.03$, $\lambda_4 = 5$.

Note that the SMFD is composed of two connected algorithms. The first one, comprising Eq. (14a) and Eq. (14b), is a second order SM based filter, responsible for rejecting of unbounded noises by filtering the error ($\mu_1 - f(t)$). The second algorithm comprises Eq. (14c) to Eq. (14e) and it is in charge of the differentiation task.

In the application under study, the first and second order derivatives of the VRFB current and voltage are required. Therefore two second order SMFD, each one in accordance with Eq. (14a) to Eq. (14e), are designed. For the current SMFD [$f(t) = I$; $L = 450A/s^2$] are used. On the other hand, for the output voltage SMFD [$f(t) = v_{out}$; $L = 300V/s^2$] are employed.

4 | RESULTS AND DISCUSSIONS

In this section, the performance of the proposed estimation methodology is thoroughly assessed and analysed via computer simulations. To facilitate comprehension, the results have been organised into two sets, covering appropriate time spans, respectively. The first set, denoted *Case Study A*, is intended to demonstrate the estimation efficiency of the proposed methodology during realistic normal operation, assuming a VRFB healthy state conditions (particularly, a negligible self-discharge rate). The second set, namely *Case Study B*, is designed to illustrate the capacity of the proposal to assess the VRFB SoH, computing three SoH indicators. To this end, a longer time span is considered and accelerated ageing/degradation factors are incorporated, to reduce the required simulation time.

For the tests, the VRFB is functioning as a stationary buffer energy storage system in an EV charging station (as introduced in Figure 1). In this hybrid system, it is assumed that the power required to charge the VRFB (P_{Bat}) is obtained from a 150KW wind energy conversion system (P_W) together with the electrical grid (P_G).

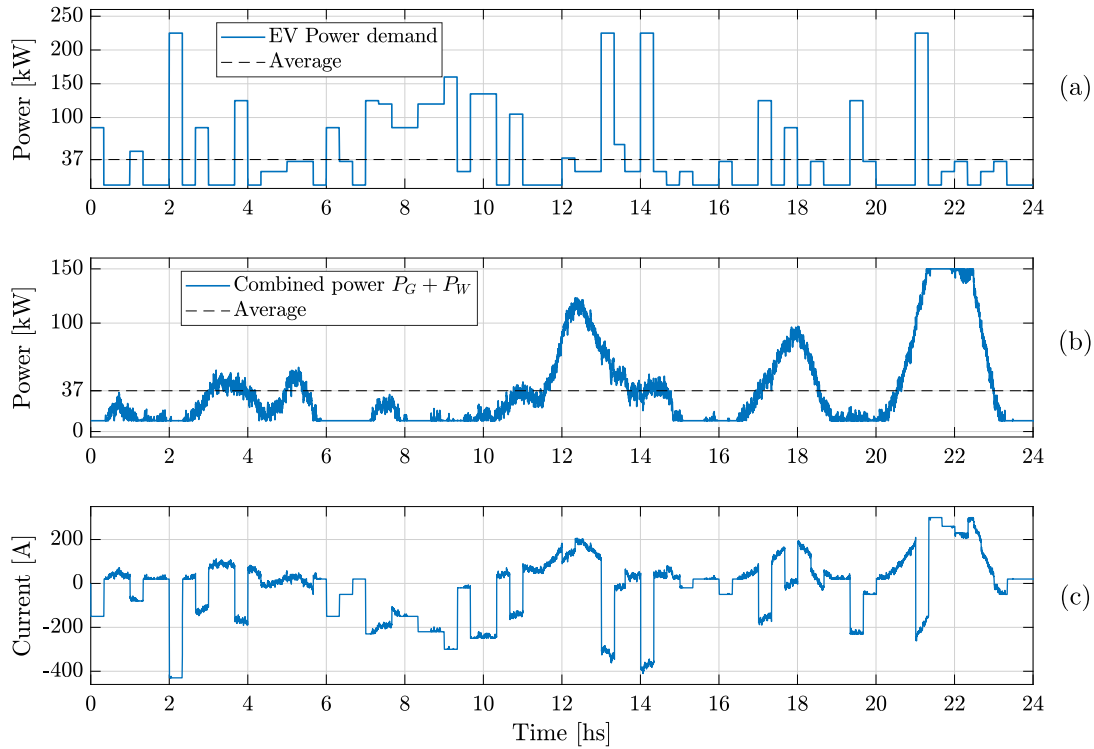


FIGURE 4 (a) EV power demand, (b) combined grid and wind energy system power, (c) resultant charge/discharge VRFB current profile.

Without loss of generality, a generic 24 hours EV charging power demand profile, suitable to illustrate the proposed methodology performance, is used (see Figure 4). The average charging time is assumed to be 20 minutes and power demand variations, ranging from 20kW to 220kW, are set. Accordingly, the VRFB's specifications are as follows:

- The rated capacity is 850Ah.
- The nominal voltage is 500V, fitting a nominal voltage of approximately 420V for the commonly employed EV Lithium-Ion batteries.
- The maximum power is 250kW, with a limit of a maximum discharge current of 500A.

The nominal values for the parameters of the ECM are: $V_0 = 390V$, $R_{ohm} = 0.05\Omega$, $R_{pol} = 0.1\Omega$, $C_{pol} = 250F$ and $R_{sd} = 560\Omega$. With regard to C_{bat} , its nominal value at $SOC = 50\%$ is $28.5kF$ (its variation is modelled with the expression $C_{bat} = \partial Q / \partial v_{oc} = 114 e^{(450-v_{oc})/27.12} / (1 + e^{(450-v_{oc})/27.12})^2 [kF]$, derived from Eq. 4 and Eq. 1). Those values have been set taking as a basis technical data reported in previous works in the field [35][36][37][38], and adapting them in accordance with the size of the VRFB under consideration [13]. Besides, to allow the illustration of the estimator tracking capability, low frequency variations were added to such nominal values to emulate realistic changes that the parameters may suffer.

4.1 | Case Study A: parameter estimation during healthy operation

In this case study, normal operation of a healthy VRFB is addressed. Therefore the self-discharge resistance R_{sd} is negligible and, consequently, the proposed 4th-order parameter estimation is utilised.

To analyse the performance of the proposed estimation methodology, a representative interval (420min to 500min) is chosen from the 24hs time-frame and is presented in Figure 5. The current and voltage profiles can be appreciated in Figure 5a and 5c. For illustrative purposes, the time-window is selected comprising periods with sufficient PE and others when it is almost nonexistent or weak. Note that, as expected, the periods with contribution of the wind turbine, result in sufficient persistence of excitation, whereas during the flat intervals (minutes 420 to 430 and 470 to 500) the methodology detects that in order to estimate, the injection of a persistent signal is required (see figures 5b and 5d). In the case under study, the injected persistent signal was generated using a PRBS appropriately filtered, to fulfil the differentiability conditions of the SMFD specified in 3.3 (see Figure 5b).

In Figure 5.d the resultant PE evaluation is shown and the $\lambda_{min}(\mathbf{R}(t))$ is presented together with the estimation thresholds. Subsequently, in Figure 5.e, the periods in which the estimation algorithm is active (i.e., when the PE conditions hold) are depicted. To visualise the accuracy of the estimated parameters, the bound for the estimation error is also displayed in the figure (orange line).

As for the values of the estimator parameters, i.e., the gain matrix G and the forgetting factor $q = 1/\tau$, they are designed by assessing the VRFB parameter variations. The forgetting factor is selected analysing the trade-off between a lengthy τ , to increase the computable data for the RLS algorithm, and a shorter one, to enhance the capability to track the VRFB time-varying parameters. For its part, the gain matrix G is designed by setting its minimum eigenvalue in accordance with the desired convergence speed, using the elements of the diagonal as weighting values. Then, after an empirical analysis based on comprehensive simulations, considering several typical current demand profiles, the following estimator parameters are chosen:

$$\mathbf{G} = 7.8 \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0.3 & 0 & 0 \\ 0 & 0 & 0.24 & 0 \\ 0 & 0 & 0 & 0.5 \end{bmatrix}; \quad q = 1/\tau = \frac{1}{29} [s^{-1}]$$

- *Parameter estimation*

The results for the electrical parameter estimation are shown in Figure 6. In order to demonstrate the robustness of the proposed methodology, additive noise was included in both, voltage and current, from minute 450 on. For the 4-th order parameter estimation, a desired precision of at least 95% is attained after a $T_e = 160s$, employing $n_\tau = 3$, $\lambda_{min}(\mathbf{G}) = 1.87$ and $\lambda_{Th} = 0.005$. The maximum Inactive Estimation Time is empirically selected considering the maximum variation rate of the ECM parameters

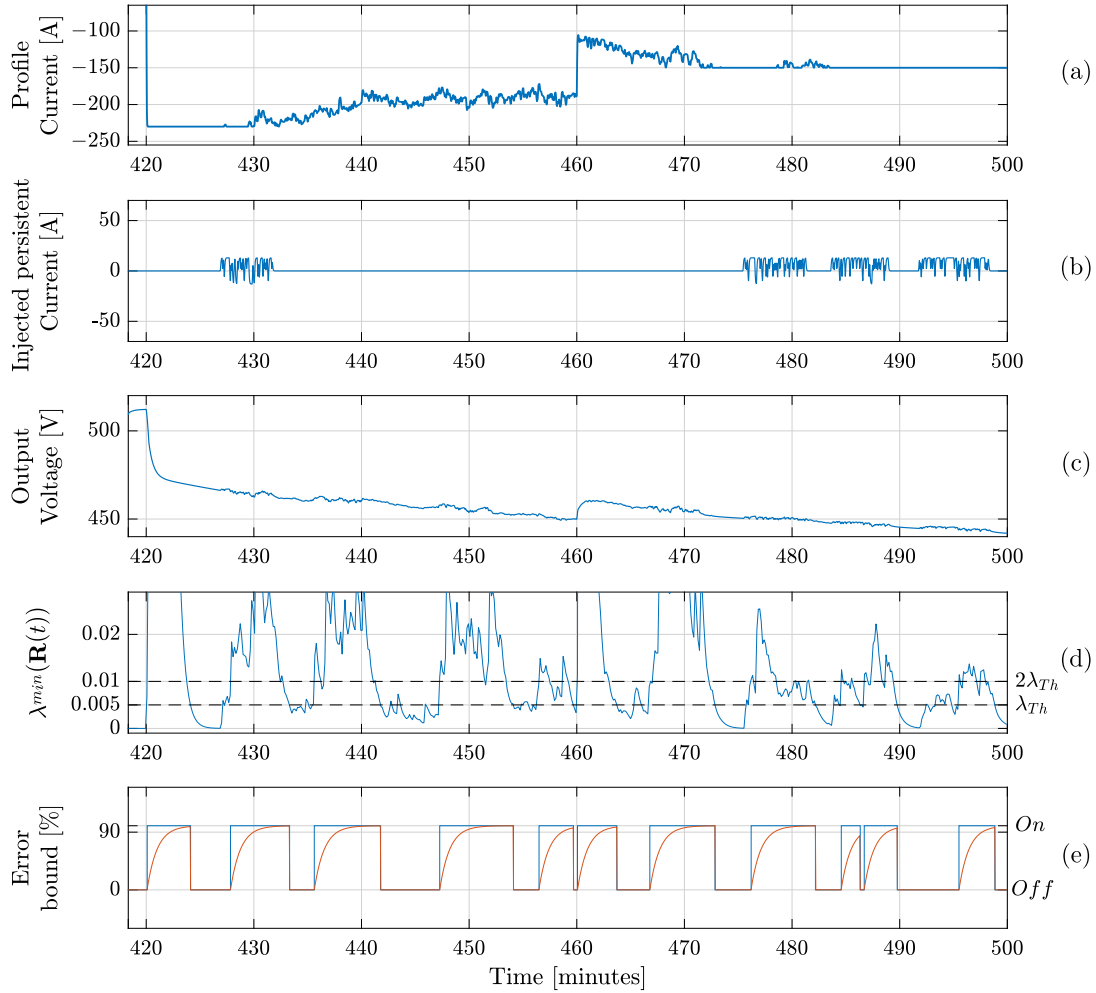


FIGURE 5 (a) VRFB current demand profile. (b) Injected persistent current. (c) VRFB output voltage. (d) $\lambda_{min}(\mathbf{R})$ for the 4-th order parameter estimation. (e) Active estimation periods and estimation precision lower bound.

and the aforementioned 95% precision. T_{imax} is computed to guarantee that the estimations will not surpass the desired 5% error bound, by avoiding inadmissible long periods without PE, resulting in $T_{imax} = 200s$. It can be observed in Figure 6 that the selected T_{imax} fulfils the desired precision even in the presence of measuring noise (see, for instance, minute 490: with no PE and consequently no estimation, the parameters do not escape the depicted error bound zones). Moreover, comparing figures 6 and 5e, it is possible to verify that the precision is always higher than the theoretical lower bound.

- *SoC computation*

To obtain the SoC of the VRFB, a procedure based on the estimation of the system's open circuit voltage v_{oc} is proposed. Since the system's description in the Fliess canonical form in Eq. (7) is known, v_{oc} can be straightforwardly inferred by computing on-line the inverse diffeomorphism from Eq. (6). Then, it is simple to solve Eq. (4) for the SoC.

Using this technique, very good results are obtained (see Figure 7). It can be observed that despite being initialised far from the real SoC, after a brief convergence lapse, the estimate proficiently tracks the actual value throughout the complete simulation

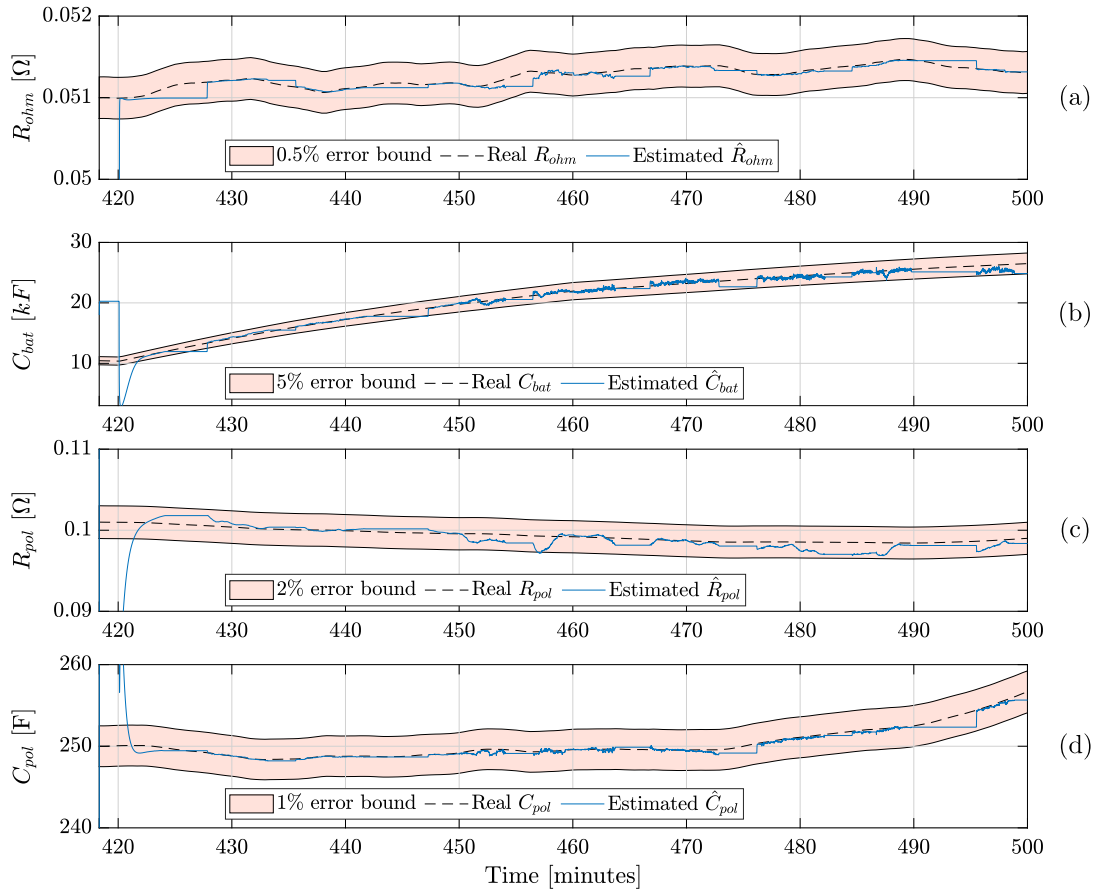


FIGURE 6 Estimated electrical parameters. An error bound is included to appreciate the estimation error.

interval. The error in the SoC estimation is consistently maintained below 0.4%, even from minute 450 on, when the effect of measuring noise can be visualised. Note that, if required, the precision of the SoC estimation could be improved if, instead of using a theoretical equation such as Eq. (4), an accurate v_{oc} -SoC look-up table obtained from experimental data is employed.

4.2 | Case Study B: detection of SoH degradation

As mentioned, the results presented in this case study focus on the assessment of the battery SoH. The latter is a figure of merit of the VRFB condition, referred to its manufacture nominal specifications. The SoH is not a single-source index, but the result of the combination of indicators or criteria, that take into account different degradation phenomena, caused by ageing or damaging events. In particular, based on the obtained estimates, three SoH indicators are considered in this paper, associated to: the charge capacity of the battery, the increase of the battery internal resistance and the self discharge rate, linked to the value of R_{sd} .

Degradation could be a slow process, involving numerous charge/discharge cycles. Therefore, to avoid extremely long simulations, degradation effects have been accelerated during *Case Study B*, by including in the tests abrupt (not necessarily realistic) variations to different critical elements of the VRFB-ECM. Similarly to *Case Study A*, an illustrative interval is selected from

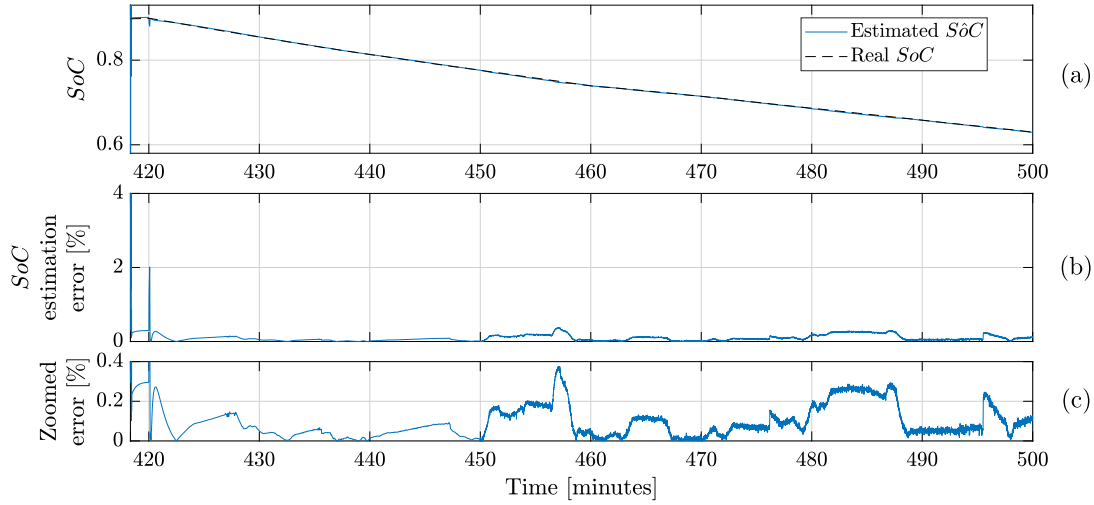


FIGURE 7 (a) Estimated and real SoC; (b) error in [%]; (c) magnified SoC estimation error.

the 24hs time-frame (Figure 4), namely from 540min to 850min, as shown in Figure 8, where the VRFB current and its output voltage are presented.

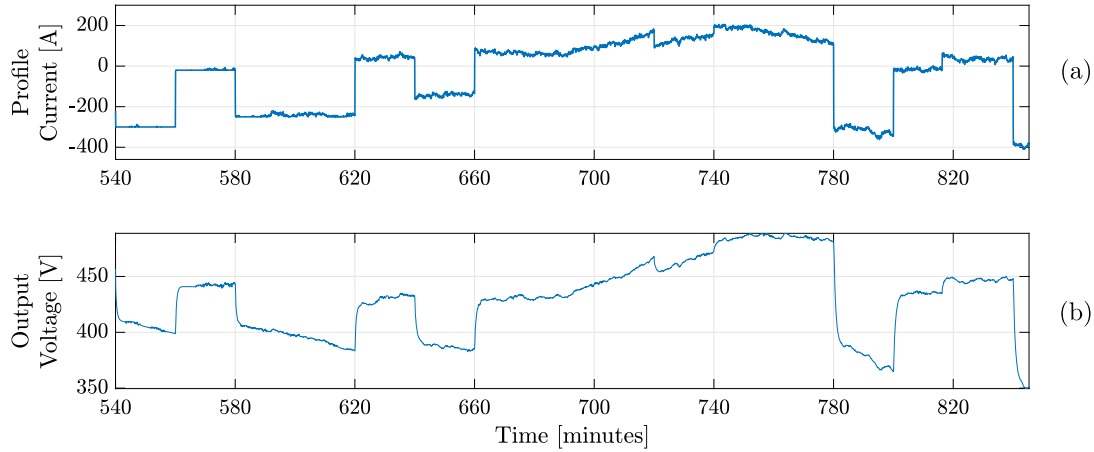


FIGURE 8 Employed profile for the *Case Study B*. In (a) the VRFB current profile is presented. In (b) the resultant VRFB output voltage is illustrated.

4.2.1 | Charge capacity fade

The charge capacity is a measure of how much energy the battery can deliver from fully charged. In VRFB, it can fade over time as a result of side reactions (hydrogen evolution, V^{2+} oxidation with atmospheric oxygen, etc.) or asymmetric diffusion of vanadium species that lead to electrolyte imbalance. Thus, this variable is a strong indication of the battery's SoH, which can be quantified by [42]:

$$SoH_Q = \frac{Q_M - Q_{Mcrit}}{Q_{Mn} - Q_{Mcrit}} \quad (15)$$

where Q_M , Q_{Mn} , and Q_{Mcrit} are the actual, nominal and critical (or minimum acceptable) capacity of the battery, respectively. In this work, the critical capacity is set $Q_{Mcrit} = 0.8Q_{Mn}$ [6]. When the charge capacity is between $0.9Q_{Mn} > Q_M > Q_{Mcrit}$ it is considered to be in a *Warning Operation Area*. Below the Q_{Mcrit} threshold, the VRFB capacity health is regarded to be compromised.

The actual capacity of the battery can be obtained from the measured current and estimated parameters of the model, as follows [42]:

$$Q_M = \frac{\int_{t_1}^{t_2} I(t)dt}{SoC(t_2) - SoC(t_1)} \quad (16)$$

Note that to increase the accuracy of the Q_M computation, the SoC difference $\Delta SoC = SoC(t_1) - SoC(t_2)$ should be set sufficiently separated, to reduce the incidence of possible SoC estimation error. In the present application, Q_M is estimated using constant intervals of $\Delta SoC = 0.1$, chosen for the illustrative purpose of displaying six Q_M estimations in the selected time window (where the SoC variation range is from 0.2 to 0.55). Observe in Figure 9a that the estimated SoC accurately tracks the real SoC, which allows an adequate computation of Eq. (16).

In this case study, to evaluate the SoH_Q two sudden drops in Q_M are introduced around minutes 590 and 715, respectively, as shown in Figure 9b. The resulting SoH_Q is presented in Figure 9c, along with the three operation areas that characterise the level of degradation of the system charge capacity.

It can be seen that the proposed method can satisfactorily track the changes in Q_M . Note that, as this criterion employs the current integral to compute Q_M , there is some delay until these variations are reflected in the estimated Q_M . However, since capacity fade is typically a slow process in comparison with the simulation time window presented in Figure 9, this delay would be nearly negligible in practice.

4.2.2 | Internal resistance increase

In VRFB, the so called internal resistance $R_i = R_{pol} + R_{ohm}$ tends to rise as the battery ages as a consequence of the electrodes and membrane degradation. Therefore, a SoH indicator related with the R_i is defined as [43]:

$$SoH_R = \frac{R_{iEOL} - R_i}{R_{iEOL} - R_{in}} \quad (17)$$

where R_{in} is the nominal internal resistance, corresponding to a new battery, and R_{iEOL} is the end-of-life internal resistance.

For the case under study, a 60% increase of the internal resistance has been set as the end-of-life threshold, i.e., $R_{iEOL} = 1.6R_{in}$. If R_i deteriorates reaching R_{iEOL} , the VRFB efficiency considerably drops. Moreover, in certain applications, the system could even be unable to supply the requested power demand.

Figure 10 displays the evolution of the SoH_R for the illustrated period. In this case, besides the previously described low frequency variation, an additional abrupt step-like failure of R_{ohm} is forced at minute 626, to allow visualisation of a SoH_R

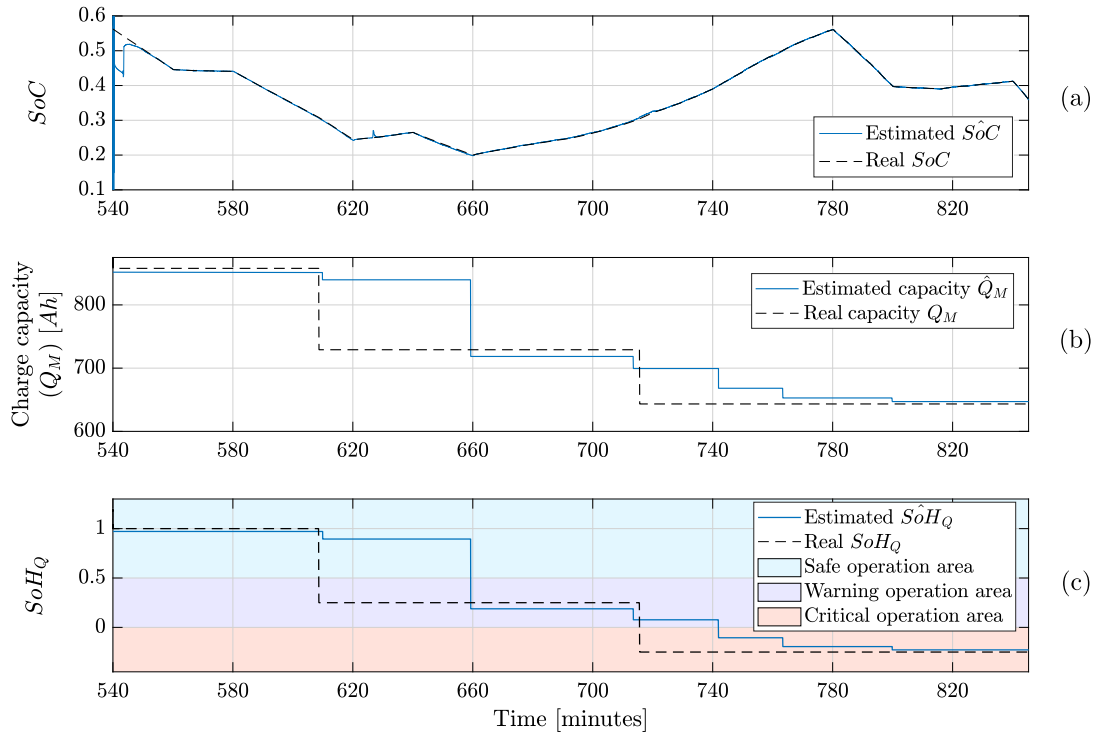


FIGURE 9 Charge capacity State of Health (SoH_Q) estimation. In (a) and (b) the variables required to perform the estimation are presented, in (c) the estimated and real SoH_Q are depicted.

change in a relative brief simulation interval. It can be appreciated how the evolution of the internal resistance is rapidly detected by the estimation method, in spite of a sudden parameter variation. After a brief transient, the estimation algorithm recovers and provides precise values for both R_i and SoH_R . Then, during the remaining of the simulation, the estimator can accurately track the rather slow variation experienced by R_i .

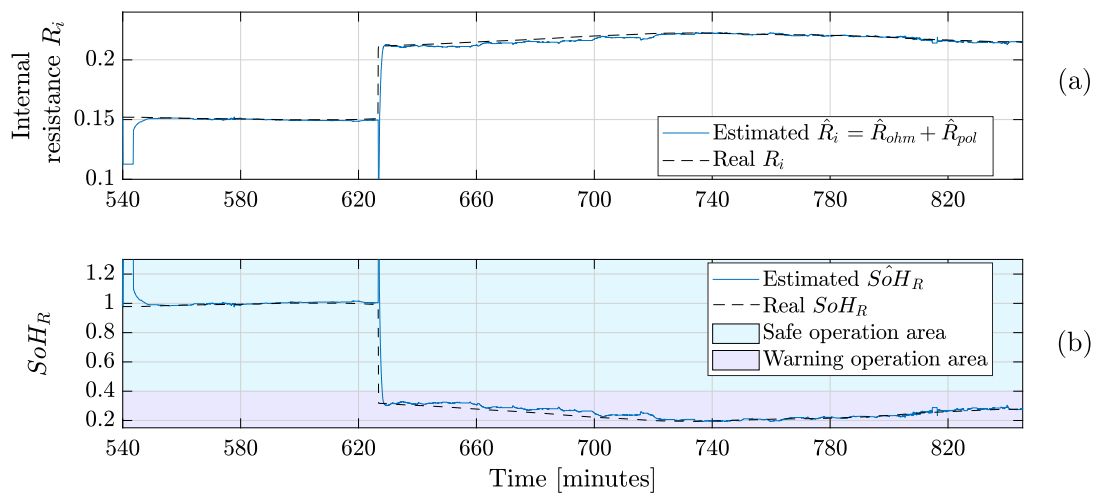


FIGURE 10 (a) Internal resistance evolution. (b) Resultant SoH_R evaluation.

4.2.3 | Self-discharge

The self-discharge of VRFB is represented with the inclusion of the R_{sd} resistance. During VRFB healthy operation, the self-discharge effect is negligible and R_{sd} is not taken into account. However, when self-discharge related degradation occurs, the associated resistance value seriously drops indicating malfunctioning of the battery. Therefore, the safe operation area can be delimited by a R_{sd} critical value, $R_{sd_{CRIT}}$, obtained from a minimum acceptable Coulombic Efficiency of the battery. Assuming the latter as 90% when the system operates with an 80kW power demand, in the system under study such delimiting value results $R_{sd_{CRIT}} = 56\Omega$. Subsequently, a health indicator SoH_{loss} is defined as follows:

$$SoH_{loss} = \frac{R_{sd_{CRIT}}}{\hat{R}_{sd}} \quad (18)$$

In the tests to reduce the simulation time, an abrupt (not realistic) self-discharge degradation is emulated in $t=690$ min, by instantaneously decreasing R_{sd} to 30Ω , going below its critical value. As previously stated in subsection 3.1, note that the 5th order estimator does not provide accurate results in brief periods, i.e. in the range of the simulation interval, when the battery is healthy with a high R_{sd} (in any case, inconsequential for the healthy VRFB model). Conversely, when the battery degrades and the resistance critically falls ($R_{sd} < R_{sd_{CRIT}}$), the precision of the estimation substantially improves, even in the short term, turning the 5th order estimator into a proficient detector of critical self-discharge conditions (as can be appreciated in Figure 11).

In the figure, the SoH_{loss} evolution, together with the $\lambda_{min}(\mathbf{R}(t))$, the active estimation periods and the achieved estimation precision, are presented. As expected, the abrupt degradation event causes the real SoH_{loss} to cross the critical limit. As soon as the PE requisite is fulfilled and the estimator is active, the estimated SoH_{loss} also enters into the critical operation area, VRFB self-discharge degradation is detected and a membrane revision is indicated.

5 | CONCLUSIONS

It has been established that the Vanadium Redox Flow Battery is an energy storage technology that possesses huge potential to be incorporated in new distributed hybrid generation systems, particularly complementing renewable energy sources. However, to turn the VRFBs into efficient and competitive ESSs, improvements are still required in several areas, such as stack design and materials, power electronics and control, and modelling and on-line battery parameter estimation.

In this paper, it was firstly proved that the latter issue can be successfully tackled through the proposed estimation methodology, based on a RLS algorithm with forgetting factor in combination with sliding mode filtering differentiators. This conjunction allowed to track the VRFB's time-varying parameters with a prescribed degree of accuracy, robustness and noise rejection capacity.

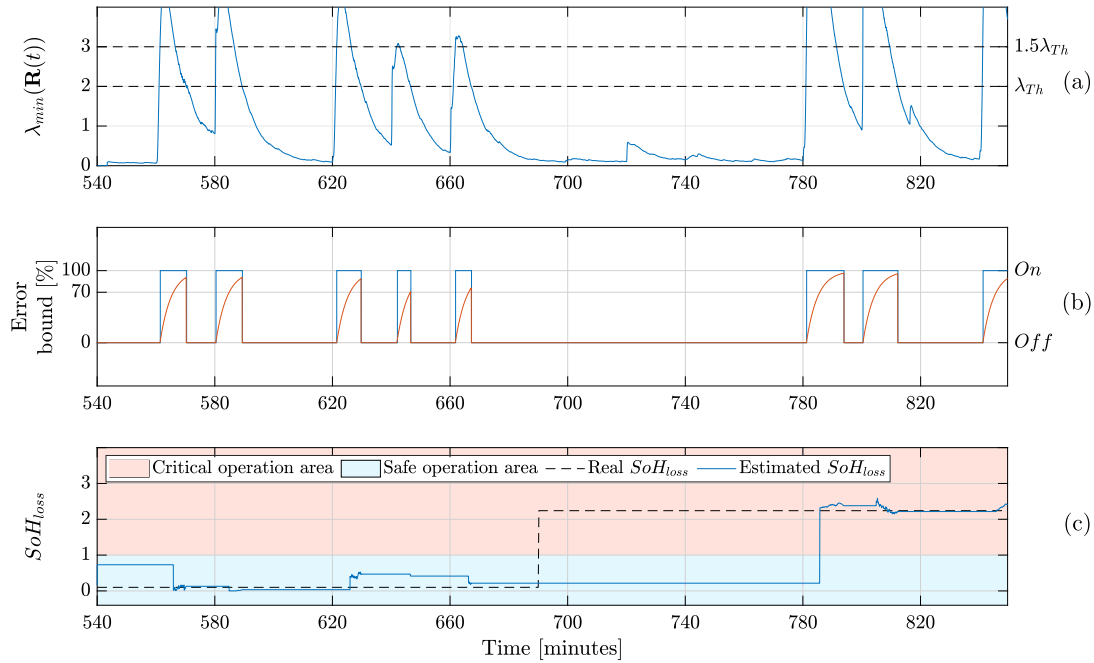


FIGURE 11 Self-discharge State of Health SoH_{loss} .

Secondly, this work was particularly focused on a topical stationary application, i.e., electric vehicles fast charging stations, a strategic field due the proliferation of EVs. The considered charging station is powered by a hybrid topology that combines a conventional grid with a wind turbine and incorporates the VRFB acting as a buffering ESS, allowing sustainability enhancement and installed power reduction.

In spite of these encouraging features, this hybrid system presented a challenge from the estimation viewpoint, due to intermittent lack of excitation persistence, for instance during periods of absence of wind. The proposed methodology overcame this problem by continuously checking the VRFB's current and voltage persistence. The goal was twofold. On the one hand, to determine the periods of sufficient PE, in order to validate the estimation. On the other hand, to detect periods of insufficient PE, hence to inject an appropriate small-magnitude persistent current signal. In both cases, the accuracy of the estimates was ensured.

Another important outcome of this research was the capacity to on-line monitoring the battery status. Based on the accurate time-varying parameter estimates provided by the proposed RLS-SMFD methodology, valuable information of the VRFB's SoC and the SoH was computed. For the SoC, a procedure based on an updated estimation of the system's open circuit voltage was utilised. For the SoH, three indicators were taken into account: the reduction of the battery maximum capacity (related to side reactions or asymmetric diffusion), the increase of the internal resistance (usually due to electrodes or membrane degradation) and the rise of the self-discharge (due to exchange membrane deficiencies). Thanks to the proposed methodology, by processing these indicators on-line, any sign of degradation could be rapidly detected.

To conclude, as future work, four main lines are being considered by the authors:

- A comparative analysis of the equivalent circuit model and the more complex electrochemical models is planned for the next stage of this research. It is of particular interest to find relations between the parameters of both models, leading to a fuller understanding of the VRFB behaviour and its characterisation. The combination of such comprehensive models with the proposed estimation methodology, will result not only in the availability of additional meaningful and thorough information of the VRFB, but also in leveraging the design of advanced controllers for the system.
- Efforts are undertaken to further improve the proposed estimation methodology. Encouraging results are being obtained regarding the reduction of the estimation time T_e , by including a time varying adaptive gain. Besides, it is also planned to explore other alternatives, such as RLS with variable forgetting factor methods or different Kalman-based estimation techniques.
- A proficient supervisory strategy to regulate the power flows between the hybrid EV charging station modules will be developed. This supervisory control setup will target performance optimisation of the system as a whole, increasing its efficiency and reliability, while extending the lifetime of the VRFB and associate devices.
- Also, it will be assessed the convenience of expanding the proposed hybrid topology, by incorporating other sustainable non-conventional energy technologies, such as solar power, as an energy source, and hydrogen/fuel cells, as a complementary storage system.

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