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A comprehensive and time efficient characterisation of redox flow batteries through Design of Experiments --Manuscript Draft--

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Abstract:	As the need for a sustainable economy rightly drives the share of renewable energy, electric grids and supporting infrastructure must flexibly adapt. As valuable building blocks in integrated systems, battery energy storage systems (BESSs) can provide the required flexibility for energy and power applications. Redox flow batteries (RFBs) are emerging as promising alternatives to lithium-ion batteries to meet this growing demand. As end-users, RFB operators must characterise the batteries to learn more about the battery's behaviour and performance and better integrate such RFB technology into energy systems. Characterisation experiments yield this information, which is essential to successfully operate and integrate redox flow battery systems. However, conducting classical characterisation protocols can take more than two weeks for large RFB modules (capacities > 30 kWh), which is too long for an efficient RFB roll-out. Better characterisation methods are required to efficiently scale up, integrate and operate RFBs in an appropriate manner. Ideally, characterisation experiments would yield a more comprehensive understanding about the battery performance and behaviour in a shorter amount of time. In order to achieve this, statistical design of experiments (DoE) is explored as an RFB characterisation tool. DoE is a statistical method that makes optimal use of the available time and resources and increases the efficiency of experiments in a statistically sound manner. Designed experiments result in empirical models for the studied system, which can predict system outputs for a vast amount of operating points. This will enable optimal operation of the battery in terms of remaining capacity management and overall electrical efficiency. Through a number of such designed experiments, dominant RFB system variables could be identified, which allow reliable modelling of the RFB performance for different charge-discharge cycles. This facilitated the design of an optimised characterisation experiment. A 50% reduction of the required RFB characterisation time is achieved and the optimal experiment yields comprehensive information about the battery performance and behaviour. As such, a shorter and better RFB characterisation procedure is realised through DoE.
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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Author Statement

Oscar Delbeke: Data curation, writing original draft, reviewing and editing, investigation, visualisation

Hannes Laget: Conceptualization, data curation, methodology, experimental setup, supervision

Simon Hollevoet: Experimental Setup, reviewing and editing, validation

Lieven Vandevelde: Reviewing and editing

Jan Mertens: Reviewing and editing, supervision

Highlights “A comprehensive and time efficient characterisation of redox flow batteries through Design of Experiments”

- Design of experiments is a suitable tool to characterise vanadium redox flow batteries.
- The method can reduce the required battery characterisation time by half.
- Designed experiments allow comprehensive modelling of battery performance.
- Designed experiments can be used for other redox flow battery chemistries as well.

A comprehensive and time efficient characterisation of redox flow batteries through Design of Experiments

Authors: *Oscar Delbeke, Hannes Laget, Simon Hollevoet, Lieven Vandevelde, Jan Mertens*

Abstract

As the need for a sustainable economy rightly drives the share of renewable energy, electric grids and supporting infrastructure must flexibly adapt. As valuable building blocks in integrated systems, battery energy storage systems (BESSs) can provide the required flexibility for energy and power applications. Redox flow batteries (RFBs) are emerging as promising alternatives to lithium-ion batteries to meet this growing demand. As end-users, RFB operators must characterise the batteries to learn more about the battery's behaviour and performance and better integrate such RFB technology into energy systems. Characterisation experiments yield this information, which is essential to successfully operate and integrate redox flow battery systems. However, conducting classical characterisation protocols can take more than two weeks for large RFB modules (capacities > 30 kWh), which is too long for an efficient RFB roll-out. Better characterisation methods are required to efficiently scale up, integrate and operate RFBs in an appropriate manner. Ideally, characterisation experiments would yield a more comprehensive understanding about the battery performance and behaviour in a shorter amount of time. In order to achieve this, statistical design of experiments (DoE) is explored as an RFB characterisation tool. DoE is a statistical method that makes optimal use of the available time and resources and increases the efficiency of experiments in a statistically sound manner. Designed experiments result in empirical models for the studied system, which can predict system outputs for a vast amount of operating points. This will enable optimal operation of the battery in terms of remaining capacity management and overall electrical efficiency. Through a number of such designed experiments, dominant RFB system variables could be identified, which allow reliable modelling of the RFB performance for different charge-discharge cycles. This facilitated the design of an optimised characterisation experiment. A 50% reduction of the required RFB characterisation time is achieved and the optimal experiment yields comprehensive information about the battery performance and behaviour. As such, a shorter and better RFB characterisation procedure is realised through DoE.

Keywords

Energy Storage, Redox Flow Battery (RFB), Design of Experiments (DoE), Characterisation, Energy Efficiency, Energy Management

1. Introduction

As the energy market is rightly transforming to become sustainable, the share of variable renewable energy is rapidly increasing. This comes with greater variations and unpredictability, which raises the need for flexibility in electric grids and supporting infrastructure [1] [2]. Scaling up stationary energy storage capacity is essential to enable the energy transition. Batteries are particularly suitable to play a crucial role in providing this flexibility, both for energy applications (e.g. time-shifting and peak shaving) and power applications (e.g. as frequency containment reserve) [3] [4].

While a great share of industrial and research focus is on Lithium-ion batteries, redox flow batteries (RFBs) are emerging as promising alternatives. As opposed to Li-ion batteries and other chemistries, active species for the RFB redox reactions are stored in the electrolytes.

The RFB working principle (schematically displayed in Figure 1) thus makes it possible to independently scale energy capacity and power of the battery, which is beneficial for its flexibility. Fast response time and power capabilities also allow redox flow batteries to be operated as frequency containment reserve (FCR). With lifetimes potentially exceeding 20 years, greater recyclability and no need for cobalt or lithium, the batteries are more sustainable than their Li-ion counterparts, as recently shown in a detailed Life Cycle Assessment study comparing both battery types [5].

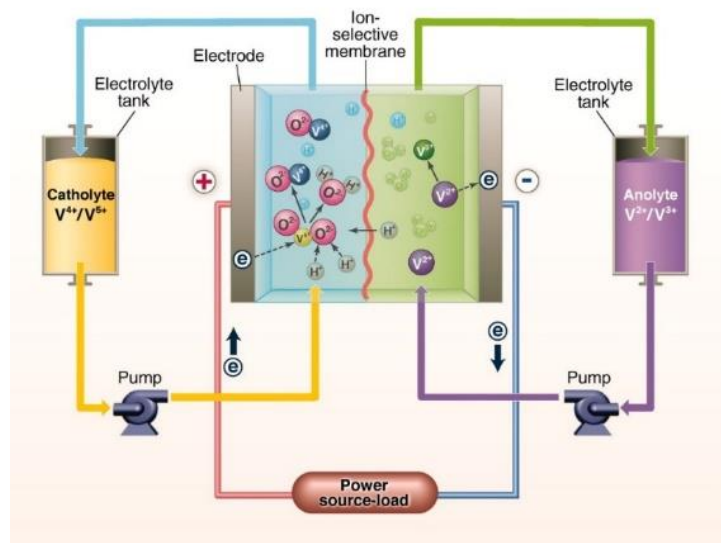


Figure 1. Redox flow battery working principle. Two half-cells circulate an electrolyte in which the active species are stored. During operation, ions migrate from one electrolyte to the other through an ion-selective membrane. This process is electrically matched by the movement of electrons through an external circuit. [6]

RFB end-users need a profound understanding of individual RFB behaviour to efficiently size, validate, integrate and operate the batteries with other systems. RFBs are therefore subjected to characterisation experiments to gain insights beyond specification sheet information. Classical characterisation procedures are essentially composed of a large number of charge-discharge cycles for which battery capacity and round trip efficiency (RTE) are measured and focus mainly on repeatability of the results. Conducting these protocols for the 30 kWh vanadium redox flow batteries (VRFBs) used in this work takes 311 hours, which is close to 13 days. The testing sequence essentially reveals the battery's RTE and full DC discharge capacity for three power ratings (nominal charge/discharge power, 2/3 nominal power and 1/2 nominal power).

While this information is indispensable, characterisation experiments should ideally yield more comprehensive information, which can be used in energy management systems (EMSs). Moreover, as longer duration batteries are needed to meet system requirements, conducting classical characterisation experiments becomes a tedious and time-consuming task since they involve repeated cycling over the full capacity range. Standard characterisation thus requires too much time for too little information, and presents a significant hurdle on the way to a more widespread and efficient implementation of RFBs.

To scale up RFB storage capacity and to efficiently integrate it into larger energy systems, there is a growing need for more time and resource-efficient characterisation experiments, especially if different use cases and possible value streams are covered with the same battery technology. Design of experiments (DoE) is therefore considered as a battery characterisation tool. DoE is a statistical technique which seeks to make optimal use of the available time and resources for experiments in general. Applying DoE to characterisation experiments would thus reduce characterisation times to a minimum, whilst obtaining the necessary information.

The data from designed experiments are used to fit empirical models which are continuous in the identified input parameters thanks to the multivariate approach. One feature of these models is that they can approximately predict system outputs (e.g. efficiency) for settings that have not been explicitly tested. In this regard, designed experiments, applied to RFBs, should outperform classical characterisation experiments, which only yield information about a limited number of operating points.

Whilst being widespread in chemical and pharmaceutical research, DoE seems to be only at the start of its potential for battery R&D, and it has only been applied to Li-ion batteries so far. For Li-ion batteries, designed experiments have been used to obtain better models, better performance and better battery designs.

Pozzi et al. [7] used designed experiments to efficiently obtain the parameters for an isothermal single particle model with electrolyte dynamics (SPMe). Su et al. [8] used designed experiments to identify the most influential stress factors affecting the cyclic ageing process in Li-ion batteries. Mathieu et al. [9] successfully used D-optimal experiments to fit a semi-empirical model derived from a polynomial approximation of a physical ageing model, which took both calendar and cyclic ageing into account. Baghdadi et al. [10] used a similar approach and further optimised it.

Boadu et al. [11] optimised the parameters for pulse-charging a lithium-polymer (LiPo) battery using design of experiments. Liu and Luo [12] similarly used designed experiments to optimise a multistage constant current (MSCC) charging method. Ryne et al. [13], Dong et al. [14] and Kim et al. [15] used DoE approaches to optimise the physical and chemical design of lithium-ion battery systems, yielding improved capacities, improved energy densities, and reduced polarisation. Lombardo et al. [16] confirm the potential of DoE for manufacturing and optimisation but are sceptical about the application range of the method. Finally, Panda et al. [17] regard DoE as “a fascinating and amazingly useful tool to enhance any study which deals with various parameters by a minimum number of experiments [...]” and consider it remarkable that experimental design is used so little in academia [17].

While DoE has yielded good results in the above mentioned works, it has not been used for redox flow batteries so far. This study is therefore the first to explore DoE for RFBs and aims to establish it as a reliable and efficient RFB characterisation tool. The main goal is to design a characterisation experiment that yields comprehensive battery information in a minimum amount of time. To this aim, this work evaluates whether or not RFB performance can be reliably modelled with a limited set of factors through DoE. DoE input and output parameters are identified based on the most relevant RFB parameters and the degree to which they can be varied by end-users. The battery itself is not modified during the experiments, only the operational parameters which are controllable by end-users. Through screening experiments, DoE is used to test the influence of these parameters and to identify the dominant parameters in the system. When the most influential parameters are identified, an appropriate and optimal characterisation can be designed. In order to validate the obtained models, their performance is evaluated on the data of the other experiments as well.

Section 2 discusses the utilised materials and methods. The experimental setup is explained and the DoE methodology is outlined. This section also details the application of DoE to RFBs, and provides an overview of the conducted experiments. Section 3 elaborates on the conducted experiments and their corresponding results. The experiments are grouped on the basis of their design. Finally Section 4 concludes with the main findings and a discussion of their implications.

2. Materials and methods

2.1 Setup

Two test setups are used. The first one consists of a single 7.5 kW – 30 kWh UET Reflex module connected to a 15 kW Victron Quattro power converter. During charging, the power converter converts 230 V AC from the grid to DC for the battery. Accordingly, the power converter converts DC from the battery to 230 V AC for the grid during discharging. The battery is controlled by an energy management system (EMS) in an external computer which also collects data from the measurements. The EMS sends power commands to the power converter and handles communication between the power converter and the battery.



Figure 2. Single RFB test setup. The battery is controlled by an energy management system in a computer, which also handles communication between the inverter (blue box) and the battery. Aside from this, the computer also collects measurements via the battery management system, which is located at the top of the RFB module.

The second setup features a string of 3 UET Reflex modules, connected in series. The modules are linked to a 90 kW Triphase power converter. The Triphase power converter is more efficient and has a faster response time compared to the power converter in the single-unit setup.



Figure 3. Series RFB test setup. Three UET RFBs are connected in series and form a string of batteries, which facilitates operation at greater voltages. The series setup has a nominal voltage of 144V and a maximum voltage of 192V.

2.2 Methodology – Design of experiments

In order to apply the DoE method, the studied system is viewed as a process with corresponding inputs and outputs. A number of controllable parameters ($x_1, x_2, \dots, x_p$) and a number of uncontrollable parameters ($z_1, z_2, \dots, z_q$) are identified in order to study their influence on the system response y . This system view is visualised in Figure 4. The selection of the controllable and uncontrollable parameters is usually based on a preliminary understanding of the system. Experimenters must be able to change the values of the controllable parameters between consecutive measurements of the system response y . Designing experiments then consists of selecting the combinations of levels for the controllable parameters ($x_1, x_2, \dots, x_p$) at which the response y must be measured. Each experiment consists of a number of tests at different combinations of levels for ($x_1, x_2, \dots, x_p$). With these measurements, an empirical model is fitted that expresses y as a polynomial function of ($x_1, x_2, \dots, x_p$) [18].

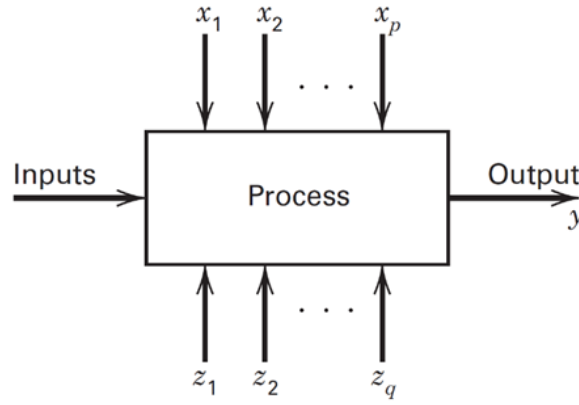


Figure 4. DoE system view. System parameters are divided in different groups. The inputs are characterised by a number of controllable parameters ($x_1, x_2, \dots, x_p$). Their effect is studied on the system outputs, which are also affected by a number of uncontrollable parameters ($z_1, z_2, \dots, z_q$). [18]

The general applicability of the method is based on the Pareto principle which proposes that any real process is mostly driven by a limited amount of important factors and Taylor's theorem which states that any function $Y = f(x_1, x_2, \dots, x_p)$ can be approached by a polynomial of first, second, ... order in an area that is sufficiently small [19].

In order to select appropriate levels for the controllable factors at which the response must be measured, an a priori model must be proposed. The selection of an adequate expression is not straightforward but can rely on two principles: the Pareto principle (or sparsity-of-effects) and hierarchy. Hierarchy entails that the variability caused by first order effects exceeds the variability that is caused by second order effects. Similarly, second order effects will have a greater influence on the system response than third order effects, and so on. This implies that before expanding the model with third order terms, second order terms should already be included [19]. These two principles (sparsity-of-effects and hierarchy) were verified and validated by Li et al. [20], who documented a meta-analysis of 113 datasets from published factorial experiments.

Once an a priori model has been proposed, which expresses an output parameter y as function of input parameters ($x_1, x_2, \dots, x_p$), the experiment can be designed according to different optimality criteria. The selected optimality criterion imposes a number of requirements on the values of ($x_1, x_2, \dots, x_p$) in the experiment, such that the resulting data provide the required information or answer the relevant questions. In this work, the D-optimality, I-optimality and orthogonality are used. D-optimality is used in order to identify the dominant parameters in the system. I-optimality is used to optimise the model predictions. Finally, orthogonality is used in order to obtain precise model parameter estimations which are mutually independent. Once the measurements of the tests have been collected, the proposed models are fitted with ordinary least squares or stepwise regression [19] [21].

The design of the experiments and the analysis of the resulting data are carried out in JMP. JMP is statistical software developed by SAS and is considered to be an excellent program by leading statisticians. A custom design platform takes into account potential resource limitations and the difficulty to change factors [18] [19]. The program puts a lot of emphasis on graphics and interactivity. This makes it easier to analyse the data and draw conclusions from it [22] [23]

2.3 DoE battery system view

The designed RFB experiments consist of a number of charge-discharge cycles for which the controllable RFB parameters are varied and for which the battery performance parameters are measured. In the experiments, each battery charge-discharge cycle is considered to be an experimental test or “run” with corresponding inputs and outputs. Many parameters have an influence on the RFB’s performance, but not all of them can be controlled by RFB end-users and operators. Table 1 provides an overview of the studied RFB parameters that may influence the battery performance, and details how they are measured or controlled. For the parameters that can be varied by RFB end-users, the lower limit and upper limit, as used in this work, are included.

Table 1. RFB parameters that may affect performance

Parameter	Measurement	Controllable by operator	Lower limit	Upper limit	Comments
Minimum state of charge (SOC)	Via open circuit voltage (OCV*)	Yes	0%	37%	Controlled through battery management system (BMS)
Maximum SOC	OCV	Yes	75%	100%	Controlled through BMS
Charge rate	N/A	Yes	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$	Controlled through BMS P_{nom} refers to the nominal RFB power, which is 7.5 kW
Discharge rate	N/A	Yes	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$	Controlled through BMS
Resting time at minimum SOC	N/A	Yes	15 min	720 min	Controlled through BMS
Resting time at maximum SOC	N/A	Yes	15 min	720 min	Controlled through BMS
Electrolyte temperature	Temperature sensor at catholyte and anolyte	No	N/A	N/A	-
Ambient temperature	Temperature sensor at top cover	No	N/A	N/A	-
Ageing and degradation	Via state of health (SOH)	No	N/A	N/A	Apart from measurements, SOH is also indicated by capacity and efficiency values
Electrolyte flow	N/A	No	N/A	N/A	Controlled through circulation pump
Electrolyte composition	N/A	No	N/A	N/A	Concentration of different compounds

*The UET Reflex RFB contains a reference cell through which smalls amounts of both electrolytes are circulated. The electrolytes remain separated, although not by an active exchange membrane. The OCV of the battery can be measured in this cell at all times. The OCV measurements are automatically compared with the SOC versus OCV curve, which is a one-on-one relationship provided by the RFB manufacturer.

Operators can set the values for the controllable parameters through the battery management system (BMS), which is the electronic system that controls the module, monitors critical parameters, protects the module from abnormal conditions and interfaces with higher level control.

Figure 5. schematically displays the nomenclature of the controllable parameters on two consecutive charge-discharge cycles. Note that the values of these parameters can be chosen and varied for each cycle by battery operators.

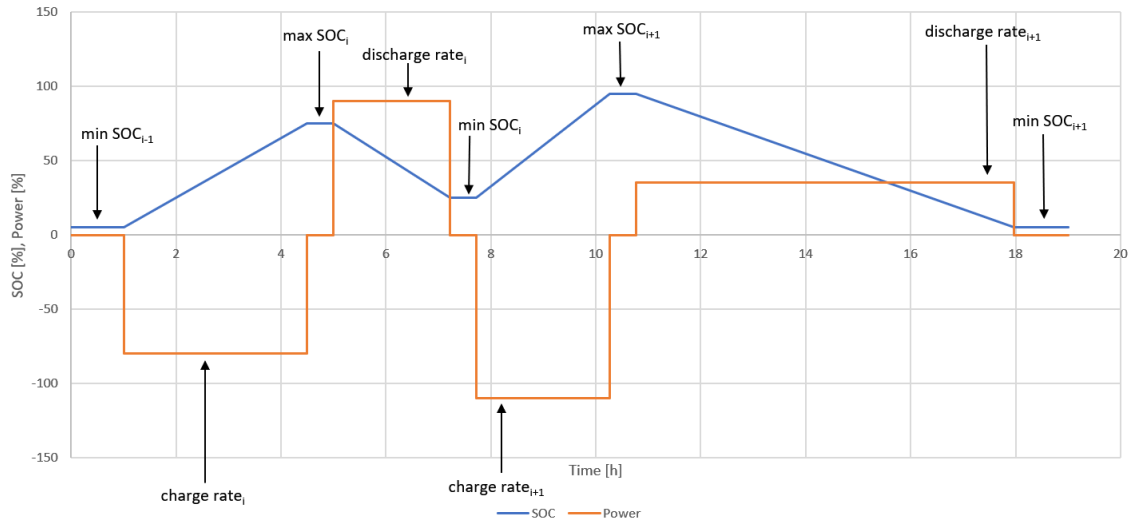


Figure 5. Charge and discharge rates (orange) and corresponding SOC variation (blue) for two consecutive charge-discharge cycles in a designed experiment.

Various parameters influence battery performance, but not all of these parameters can be controlled by RFB operators. As such, their values can not be actively altered between consecutive experimental runs, which makes it impossible to include them in the design of the experiments. Other parameters do not vary considerably throughout the experiment. As a consequence, it does not make sense to include them in the models either since their values do not vary in a range that is large enough to reliably model them. The only exception to this is the electrolyte temperature, which varies in a considerable window throughout the measurements. Its effect on the battery performance is discussed in Section 3, under Designs A and C.

The studied RFB output parameters are the corrected DC discharge capacity and the DC RTE, calculated with corrected charge and discharge capacities. As a result of actively varying minimum SOC and maximum SOC values, the charge and discharge capacities change between consecutive cycles. Therefore, in order to compare battery performance for different cycles, the charge and discharge capacities are scaled such that the corrected capacities correspond to complete charge-discharge cycles (SOC: 0 → 100% → 0). Based on the corrected DC capacities, the corresponding DC RTE for a cycle i is defined as:

$$\eta_{DC,i} = \frac{\text{Scaled DC discharge capacity}_i}{\text{Scaled DC charge capacity}_i} \quad (1)$$

The DC RTE can vary between 0 and 1. Note that the auxiliary power required to feed the pumps of the RFB (500 W) is implicitly excluded from the efficiency calculation. The pumps also keep circulating the electrolyte while the battery is at rest. Note that this is a manufacturing decision and therefore outside the control of RFB end-users.

When the system view of Figure 4 is applied to the UET Reflex module (the RFB under study), Figure 6 is obtained by using the parameters from Table 1.

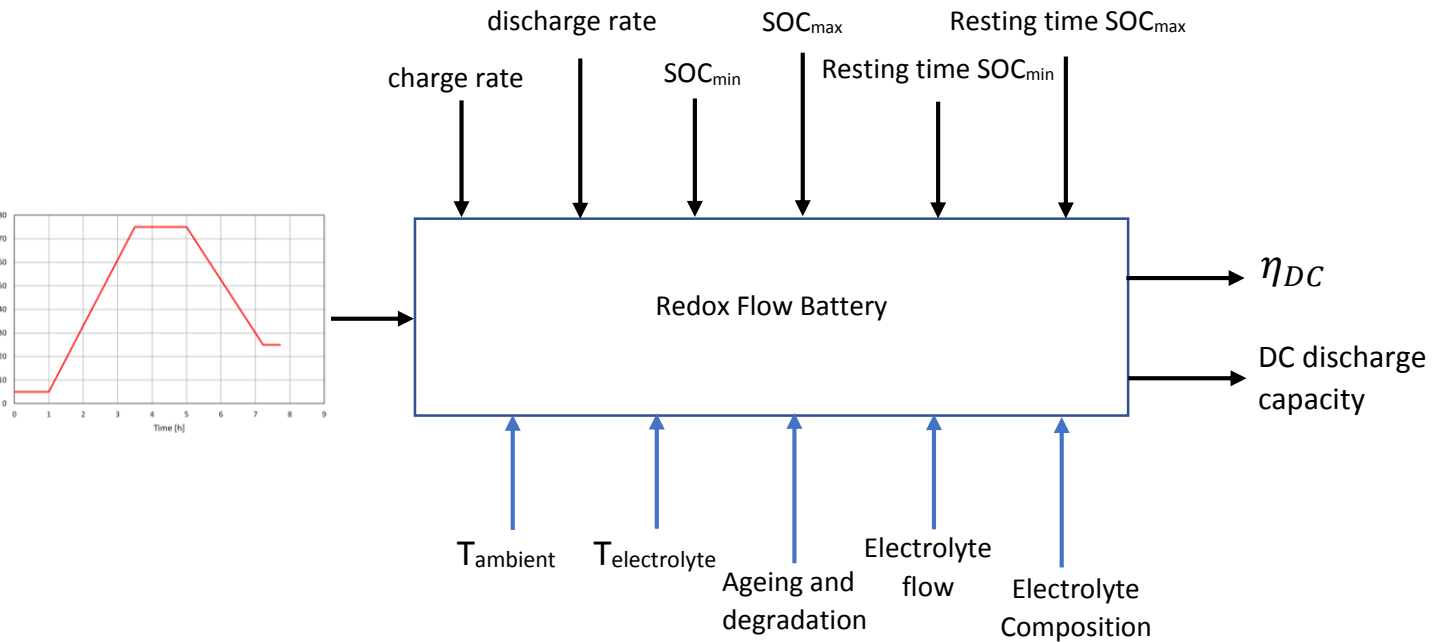


Figure 6. Redox flow battery system view. System parameters are divided in different groups. The inputs (left of the box) translate to charge-discharge cycles for the RFB, which are characterised by a number of controllable parameters (on top of the box). Their effect is studied on the system outputs (right of the box) which are also likely affected by a number of uncontrollable parameters (below the box).

2.4 Overview of the experiments

Table 2 provides an overview of the designed experiments that were performed and their corresponding durations, with the ranges of the parameters that are varied between the cycles. The design of the experiments is explained in Section 3. Design 0 is not designed with DoE but denotes the characterisation experiment corresponding to the standard protocol. It is briefly discussed in the next section to facilitate comparison with the designed experiments.

Table 2. Overview of the designed experiments

Design	Setup	Design criterion	Duration [h]	Parameters	Lower limit	Upper limit
0	Single UET	Standard protocol	311	Power rating	$0.5 \cdot P_{nom}$	P_{nom}
A	Single UET	D-optimality	204	Charge rate	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$
				Discharge rate	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$
				Minimum SOC	0%	25%
				Maximum SOC	75%	100%
B	Series UET	D-optimality (16 runs)	260	Charge rate	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$
				Discharge rate	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$
		D+I-optimality (27 runs total)	370	Minimum SOC	5%	37%
				Maximum SOC	75%	95%
C	Single UET	D-optimality	476	Charge rate	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$
				Discharge rate	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$
				Minimum SOC	5%	25%
				Maximum SOC	75%	95%
				Resting time Minimum SOC	0.5 h	12 h
				Resting time Maximum SOC	0.5 h	12 h
D	Single UET	Orthogonality	155	Charge rate	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$
				Discharge rate	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$
				Minimum SOC	0%	37%
				Resting time Maximum SOC	0.5 h	4 h

3. Results and discussion

Experiment 0

Experiment 0 denotes the classical characterisation experiment which follows the standard characterisation protocol. This experiment essentially reveals the battery's RTE and full discharge capacity for three power settings (nominal charge/discharge power, 2/3 nominal power and 1/2 nominal power), which are equal for charging and discharging. Conducting standard characterisation protocols for the 7.5 kW – 30 kWh UET Reflex modules takes 311 hours, which is close to 13 days.

The standard characterisation revealed that the UET Reflex modules considerably outperform their specification sheet values, both in terms of DC RTE and DC discharge capacity. While the specification sheet DC RTE and DC discharge capacity are reported to be 80% and 30 kWh at nominal power respectively, measurements up to 82% and 34 kWh for these respective parameters were obtained.

Designed experiments

Through 7 experiments conducted on the single RFB module and 3 experiments conducted on the string of RFB modules connected in series, the dominating factors affecting the battery performance could be identified and confirmed. Once these most influential parameters were identified, appropriate model expressions for the DC RTE and DC discharge capacity could be formulated. These expressions facilitated the design of an optimal characterisation experiment, which outperforms standard characterisation protocols both in terms of experimentation time and in terms of the quality of the resulting information. The experiments are discussed in groups. Sections A, B, C and D each discuss a number of experiments which follow a similar design or reasoning.

Design A

The first four experiments were conducted on the single RFB module following a D-optimal design scheme. They are meant to identify the most influential controllable parameters in the system. The D-optimality criterion is used since it is ideal for screening experiments, which are used to identify the dominant factors in a system. Moreover, D-optimality maximises the information gained from the experiment [19] [21]. An elaborate explanation about the mathematical background of this approach, based on the Fisher information matrix has been published by Fedorov 1972 [24].

The experiments were designed to fit and test the a priori models displayed in Equations 2 and 3, which include four of the six controllable parameters of Table 1. The models only include controllable parameters for the reasons detailed in Section 2.3. Designing an experiment based on a model requires selecting the settings for the system parameters at which the response must be measured. This is not possible for uncontrollable parameters, of which the settings can not be controlled. The resting times at minimum and maximum SOC are not included in these models because they were thought to be insignificant at this stage. The experiments of Design C (below) have refuted this assumption however.

$$\begin{aligned}\eta_{DC} = & \beta_{\eta,0} + \beta_{\eta,1}CR + \beta_{\eta,2}DCR + \beta_{\eta,3}SOC_{\max} + \beta_{\eta,4}SOC_{\min} + \beta_{\eta,5}CR \cdot DCR \\ & + \beta_{\eta,6}CR \cdot SOC_{\max} + \beta_{\eta,7}CR \cdot SOC_{\min} + \beta_{\eta,8}DCR \cdot SOC_{\max} \\ & + \beta_{\eta,9}DCR \cdot SOC_{\min} + \beta_{\eta,10}SOC_{\max} \cdot SOC_{\min} + \beta_{\eta,11}CR^2 + \beta_{\eta,12}DCR^2 \\ & + \beta_{\eta,13}SOC_{\max}^2 + \beta_{\eta,14}SOC_{\min}^2\end{aligned}\quad (2)$$

$$\begin{aligned}
\text{DC Discharge Cap.} = & \beta_{\text{cap},0} + \beta_{\text{cap},1}\text{CR} + \beta_{\text{cap},2}\text{DCR} + \beta_{\text{cap},3}\text{SOC}_{\text{max}} \\
& + \beta_{\text{cap},4}\text{SOC}_{\text{min}} + \beta_{\text{cap},5}\text{CR}\cdot\text{DCR} + \beta_{\text{cap},6}\text{CR}\cdot\text{SOC}_{\text{max}} \\
& + \beta_{\text{cap},7}\text{CR}\cdot\text{SOC}_{\text{min}} + \beta_{\text{cap},8}\text{DCR}\cdot\text{SOC}_{\text{max}} + \beta_{\text{cap},9}\text{DCR}\cdot\text{SOC}_{\text{min}} \\
& + \beta_{\text{cap},10}\text{SOC}_{\text{max}}\cdot\text{SOC}_{\text{min}} + \beta_{\text{cap},11}\text{CR}^2 + \beta_{\text{cap},12}\text{DCR}^2 \\
& + \beta_{\text{cap},13}\text{SOC}_{\text{max}}^2 + \beta_{\text{cap},14}\text{SOC}_{\text{min}}^2 \quad (3)
\end{aligned}$$

In the models, the charge rate, the discharge rate, the minimum SOC and the maximum SOC are denoted as CR, DCR, SOC_{min} and SOC_{max}, respectively. The β 's represent the model parameters that need to be estimated with the experimental data. The models are structured such that they include an intercept (β_0), first order terms and second order terms (two-factor interactions ($x_i \cdot x_j$) and quadratic effects (x_i^2)). As such, the a priori models are based on the sparsity-of-effects and hierarchy principles discussed in Section 2.2. The sparsity principle is applied by only including the few controllable factors which are likely to exert a significant influence on the RFB performance. Hierarchy is respected such that only the first and second order terms of the selected parameters are included, which will cause greater variability than higher order terms of the same parameters. If the second order terms are found to be highly significant, the model will be expanded with third order terms.

To gain insight into the relative importance of the factors, they are ranked on the basis of their corresponding p -values. In order to define the p -value, consider the test statistic β_i (a model coefficient) and a null hypothesis stating $\beta_i = 0$. The p -value is then defined as "the probability of obtaining a value for the test statistic that is as extreme or more extreme than the value actually observed." [25] The probability is calculated under the null hypothesis. The lower the p -value, the lower the probability that the observed parameter value would be obtained under the null hypothesis. This means that there is a lower chance of the null hypothesis being true and thus a higher chance of β_i differing from 0. This in turn implies that the factor has a higher likelihood of actually being significant in the system. Factors for which the p -value is lower than 0.05 are considered to be significant. This is common practice in statistics [19].

Insignificant factors are excluded as much as possible in order to get compact, reliable models. If the quadratic term of a factor turns out to be significant however, the corresponding linear term is also included in the model, following the hierarchy principle.

For the DC RTE, the statistically dominant effects turned out to be the discharge rate, the charge rate and the electrolyte temperature. Although the electrolyte temperature is not a controllable factor, it is easy to measure and the experiments demonstrated that including a temperature term in the models can significantly improve their prediction capabilities. This requires that the electrolyte temperature varies sufficiently throughout the measurements. The ranking of the effects on the basis of their corresponding p -values is displayed in Figure 7.

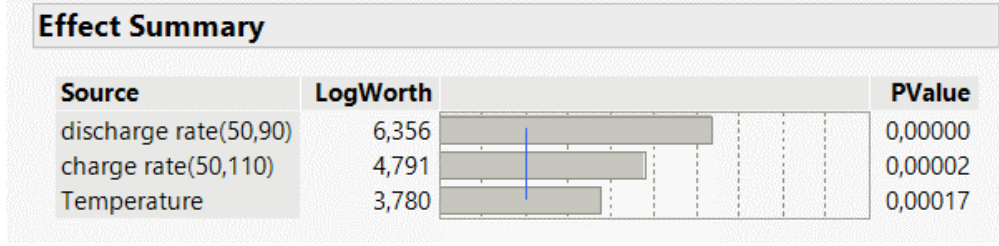


Figure 7. Dominant effects affecting the DC RTE in the first experiments, following Design A.

No significant two-factor interactions ($x_i \cdot x_j$) or quadratic effects (x_i^2) were detected, and the minimum and maximum SOC of the cycle seemed to be of lesser importance.

In the scope of this work, only quantitative continuous factors are included in the models. Since these system inputs vary in different ranges, estimates of the model coefficients can vary greatly. Coding the factors makes it possible to see the relative importance of the effects at first glance. As an example, the coding for the charge rate term in the model is given. If a factor varies between a lower end point L and an upper end point U , the interval $[L, U]$, or [50%, 110%] for the charge rate, is transformed to $[-1, +1]$ according to:

$$M = \frac{L + U}{2} = \frac{50 + 110}{2} \quad (4)$$

$$\Delta = \frac{U - L}{2} = \frac{110 - 50}{2} \quad (5)$$

$$x_k = \frac{l_k - M}{\Delta} = \frac{l_k - 80}{30} \quad (6)$$

Here, M is the midpoint of the original interval and Δ represents half of its range. In scaled values, x_k will vary linearly between its low level -1, corresponding to the original L , and its high level +1, corresponding to the original U [19]. This leads to the following model for the RTE, which is fitted with ordinary least squares and expressed with coded terms:

$$\eta_{DC} = 0.77487 - 0.014986 \left(\frac{CR - 80}{30} \right) - 0.020247 \left(\frac{DCR - 70}{20} \right) + 0.0029175 \cdot T \quad (7)$$

The quality of the obtained models is evaluated by using the coefficient of determination R^2 and the root mean square error RMSE.

The coefficient of determination R^2 is the fraction of the variation in the data that can be explained by the obtained regression model. It is calculated by comparing the regression sum of squares SSR with the total sum of squares SSTO in the data. The regression sum of squares can also be written as one minus the error sum of squares SSE, as denoted in the following equation:

$$R^2 = \frac{SSR}{SSTO} = 1 - \frac{SSE}{SSTO} = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (8)$$

In this expression, $\hat{y}_i$ represents the prediction of the model for measurement y_i and $\bar{y}$ represents the average value of the measurements. For a perfect model, there are no errors on the predictions and the R^2 equals one. Note that R^2 can even be negative, indicating that the sum of squared errors is larger than the total sum of squares, and the model yields worse predictions than a horizontal line on the average response [21].

Finally the root mean square error RMSE is used to indicate how far the predictions are off on average. It serves as an estimation of the standard error on the predictions of the actual observations [18].

$$\text{RMSE} = \sqrt{\sum_{i=1}^n \frac{(\hat{y}_i - y_i)^2}{n}} \quad (9)$$

The model performance was also evaluated by applying the models to the data of other experiments. Ideally, the R^2 and RMSE values calculated on a new dataset should be close to the R^2 and RMSE values for the dataset on which the model was originally fitted.

The R^2 and the RMSE of the efficiency model of equation (7) respectively amount to 0.934 and 0.00679. The R^2 indicates that 93.4% of the variation in the data can be explained by the model. Furthermore, the RMSE indicates that the predictions are only 0.679% off on average, which amounts to a 0.78% relative error compared to the average efficiency of the experiment.

For the DC discharge capacity, the following dominant effects were identified on the basis of their corresponding p -values: the discharge rate, the squared minimum SOC and the electrolyte temperature. The discharge capacity model is obtained accordingly:

$$\begin{aligned} \text{DC Discharge cap.} = & 41400.6 - 1262.1 \left(\frac{\text{DCR} - 70}{20} \right) - 140.31 \left(\frac{\text{SOC}_{\min} - 12.5}{12.5} \right) \\ & + 201.72 \left(\frac{\text{SOC}_{\min} - 12.5}{12.5} \right)^2 - 189.98 \cdot T \end{aligned} \quad (10)$$

With an R^2 of 0.957 and a RMSE of only 256 Wh, this model shows an excellent fit on the experimental data. Since the squared minimum SOC is statistically significant, its corresponding linear term is also included in the model despite being statistically insignificant. This way, the hierarchy principle is respected. No other quadratic effects or significant two-factor interactions were detected for the DC discharge capacity.

Design B

The experiments discussed in this section were executed on the series RFB setup and are designed with the same controllable parameters as experiment A. As a first experiment, a D-optimal design similar to Design A was conducted on the series RFB setup. Later, an I-optimal 8-run extension to the original experiment was conducted as a separate experiment. The I-optimal extension is added in order to study the potential improvement of the models. If it is fairly certain that an expression is appropriate to model a system, I-optimality can be used to optimise the prediction accuracy of the empirical model by minimising the variance of the predictions over the entire experimental region, relative to the variance of the statistical error on the model predictions, σ_ϵ^2 [18] [19]. Finally, both (D- and I-optimal) designs were conducted as consecutive parts of one experiment, which is discussed below. The D-optimal part of the experiment took about 260 hours. The complete experiment took 370 hours.

Following the same procedure as discussed for Design A, a DC efficiency model is obtained. The significant parameters are the charge rate, the discharge rate, the minimum SOC and the maximum SOC. Likewise, the DC discharge capacity model is composed of terms for the charge rate, the discharge rate, the maximum SOC, the minimum SOC and quadratic terms for the maximum and the minimum SOC.

The data indicate that the change in R^2 due to the I-optimal extension is negligible but that a relative reduction of 17% and 8% of the RMSE is achieved for the DC RTE and the DC discharge capacity model, respectively.

Since the RMSE serves as estimator for the standard deviation on model predictions, an approximated probability distribution function (PDF) for the actual output values can be plotted based on its value. Figure 8 displays the effect of the reduced RMSE on the PDF for the actual output value, when the model predicts an output that corresponds to the mean of experiment B. The green lines correspond to the models fitted on the original D-optimal runs while the red lines correspond to the models fitted on the complete experiment.

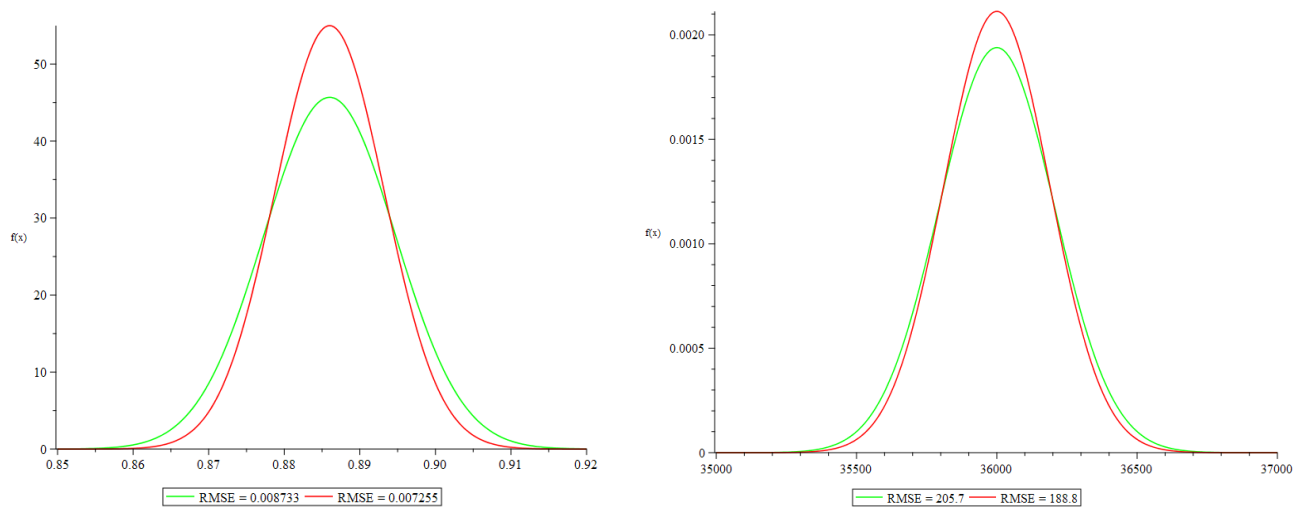


Figure 8. Small improvement of the added runs on the approximated probability distribution function of model predictions for the DC RTE (left) and the DC discharge capacity (right). The green lines correspond to the PDF of the models fitted on the original D-optimal runs. The red lines correspond to the models fitted on the complete experiment.

The improvement of the models due to the extra runs is limited, which is also visible in Figure 7. It is therefore concluded that the I-optimal extension to the original D-optimal experiment is not worth the extra experimentation time, which amounts to 110 hours.

Design C

While the models of experiment A include a significant temperature term, the capacity model of experiment B yielded good results without one. With the data so far, the influence of the electrolyte temperature on the RFB performance parameters is not clear. For batteries in general, the electrolyte temperature plays an important role. Since the temperature is not actively regulated for redox flow batteries, finding an appropriate way to quantify its influence on the battery performance is particularly important.

From a physical point of view, it makes sense that the electrolyte heats up faster when the battery operates at higher power ratings over large SOC ranges. Part of the temperature influence is thus indirectly quantified in the models already. To gain a better understanding of the temperature effect, resting times are varied in this experiment. This way, the electrolyte can cool off and the process can be quantified with controllable factors. The experiment is performed on the single RFB setup.

The resting times are varied between 15 and 720 minutes (12 hours). Since a redox flow battery has a considerable thermal inertia, the waiting times are varied over a large range in order to get a clear image of their effect on the RFB outputs. The resting time at minimum SOC for a cycle ($\text{Restingt}_{\text{SOC,min}}$) is defined as the time the battery remains at the minimum SOC of the previous cycle. This factor is meant to quantify the influence of the amount of time between subsequent cycles. The resting time at maximum SOC ($\text{Restingt}_{\text{SOC,max}}$) on the other hand is the amount of time between the charge and the discharge of a cycle. The parameters are schematically displayed in Figure 9. The experiment has a 16-run D-optimal design, which includes active variation of all six controllable parameters. As such, the experiment is meant to detect which of the controllable parameters have the most significant effect on the studied performance parameters.

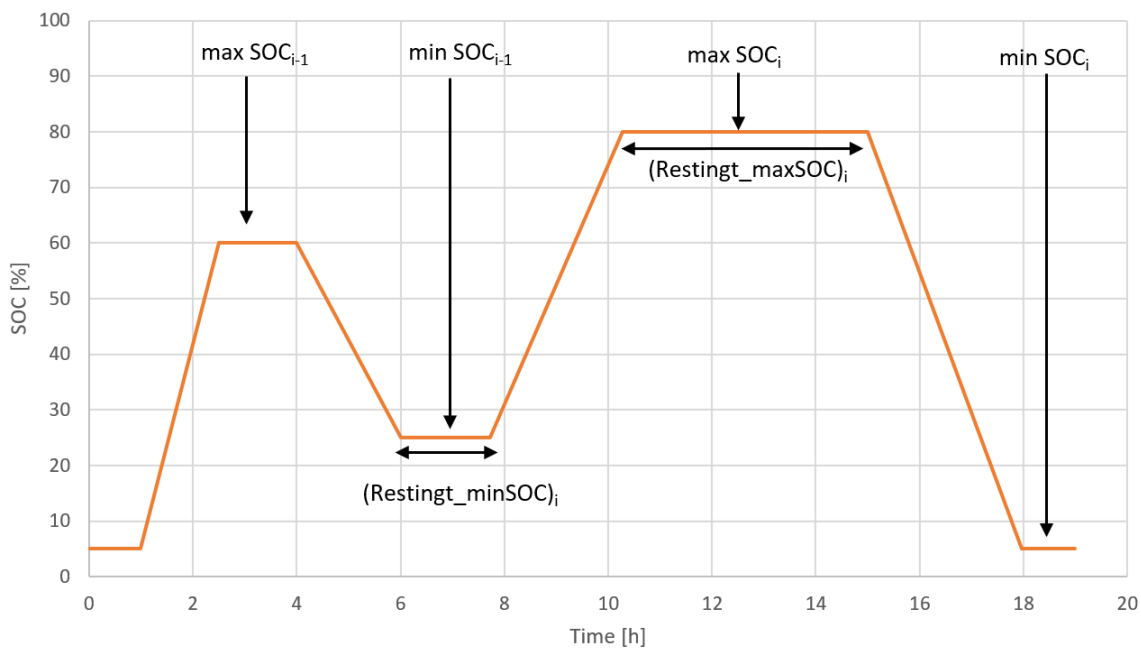


Figure 9. Definition of the resting times on the SOC curve for two consecutive charge-discharge cycles.

In this experiment, the resting time at maximum SOC was detected as a statistically significant parameter for predicting the DC efficiency and the DC discharge capacity. As discussed in Section 2.3, the pumps keep the electrolytes circulating, even when the battery is at rest. As such, the electrolytes are kept homogeneous throughout the experiment, also during rest. This may explain why the resting time at maximum SOC is found to be statistically significant. Following the same procedure as discussed for Design A, a DC efficiency model is obtained which includes terms for the charge rate, the discharge rate, the resting time at maximum SOC and the electrolyte temperature. This model attains an R^2 of 0.957 and an RMSE of 1.46% on the data of Experiment C.

Likewise, the DC discharge capacity model features terms for the discharge rate, the resting time at maximum SOC and the electrolyte temperature. It yields an R^2 and an RMSE of 0.959 and 406 Wh respectively. Throughout the experiments, it became clear that a temperature term only provides added value to the models if the temperature range is considerable for the experiment (ideally it varies between the extremes of 20°C and 38°C). This implies that in order to fully capture the effect of the temperature on the DC RTE and the DC discharge capacity, the battery should not be operated for a number of days before the start of the characterisation experiment. This way, the electrolyte temperature can be close to ambient temperature at the start of the experiment, and can vary over a large range during the RFB characterisation.

Design D – The optimally designed characterisation experiment

With the insights from Designs A, B and C, the most influential controllable parameters were identified. Based on this selection, the following expressions are formulated, which can adequately model the RFB performance parameters with only a limited set of variables.

$$\eta_{DC} = \beta_{\eta,0} + \beta_{\eta,1} \left(\frac{CR - 80}{30} \right) + \beta_{\eta,2} \left(\frac{DCR - 70}{20} \right) + \beta_{\eta,3} \left(\frac{RT_{SOC_{max}} - 127.5}{112.5} \right) + \beta_{\eta,4} \left(\frac{SOC_{min} - 12.5}{12.5} \right) + \beta_{\eta,5} \cdot T \quad (11)$$

$$\text{DC Discharge Cap.} = \beta_{cap,0} + \beta_{cap,1} \left(\frac{DCR - 70}{20} \right) + \beta_{cap,2} \left(\frac{RT_{SOC_{max}} - 127.5}{112.5} \right) + \beta_{cap,3} \left(\frac{SOC_{min} - 18.5}{18.5} \right) + \beta_{cap,4} \cdot T \quad (12)$$

Based on these models, a corresponding orthogonal characterisation experiment could be designed which only takes 155 hours (6.5 days) to conduct. Orthogonal experiments are designed such that the variances of the parameter estimates for the model, $\text{var}(\hat{\beta}_i)$, are as small as possible and the parameter estimates are mutually independent [19]. As such, the designed orthogonal experiment results in the essential data to fit the models in Equations 11 and 12 and makes sure that the model predictions are as precise as possible. At the same time, the orthogonality criterion ensures that the data is obtained in a minimum amount of time, therefore keeping the experiment as short as possible. A summary of the significant factors from each experiment and the corresponding R^2 and RMSE of the DC RTE models and the DC discharge capacity models is provided in Tables 3 and 4 respectively.

Table 3. Significant parameters and corresponding R^2 and RMSE of the obtained DC RTE models.

Design	Setup	Significant parameters (included in the models)	R^2	RMSE [–]
A	Singe UET	Charge rate, discharge rate, electrolyte temperature	0.934	0.00679
B D – optimal runs	Series UET	Charge rate, discharge rate, maximum SOC, minimum SOC	0.978	0.00873
B D + I – optimal runs	Series UET	Charge rate, discharge rate, maximum SOC, minimum SOC	0.978	0.00726
C	Single UET	Charge rate, discharge rate, resting time maximum SOC, electrolyte temperature	0.957	0.0146
D	Single UET	Charge rate, discharge rate, resting time maximum SOC, minimum SOC, electrolyte temperature	0.860	0.0190

Table 4. Significant parameters and corresponding R^2 and RMSE of the obtained DC Discharge Capacity models.

Design	Setup	Significant parameters (included in the models)	R^2	RMSE [Wh]
A	Singe UET	Discharge rate, minimum SOC, squared minimum SOC, electrolyte temperature	0.957	256
B D – optimal runs	Series UET	Charge rate, discharge rate, maximum SOC, minimum SOC, squared maximum SOC, squared minimum SOC	0.987	206
B D + I – optimal runs	Series UET	Charge rate, discharge rate, maximum SOC, minimum SOC, squared maximum SOC, squared minimum SOC	0.982	189
C	Single UET	Discharge rate, resting time maximum SOC, electrolyte temperature	0.959	406
D	Single UET	Discharge rate, resting time maximum SOC, minimum SOC, electrolyte temperature	0.980	213

In order to visualise the quality of the models that are obtained from the optimal characterisation experiment, Figure 10 demonstrates the measured versus the predicted values of the performance parameters on the data of Design D.

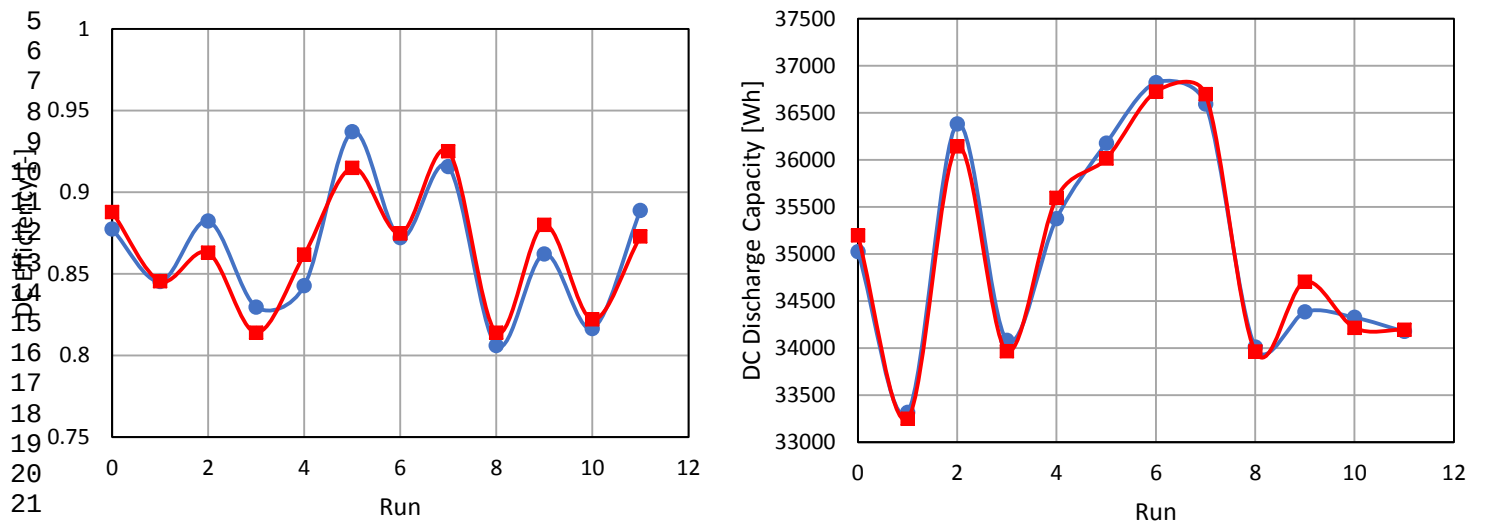
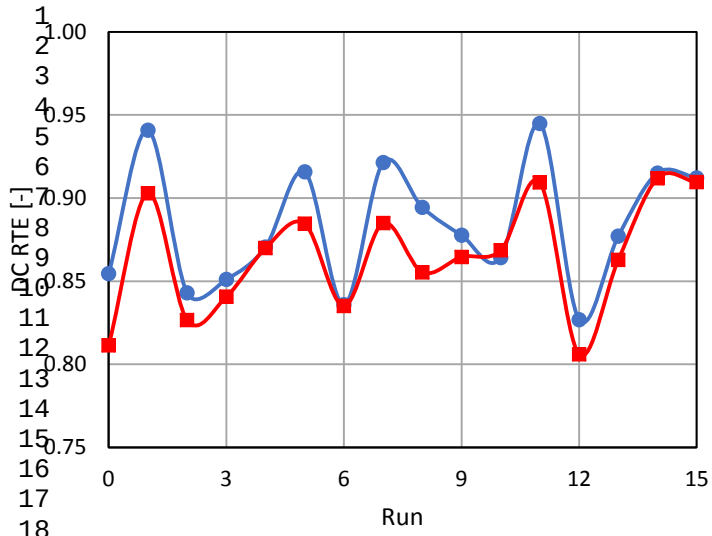
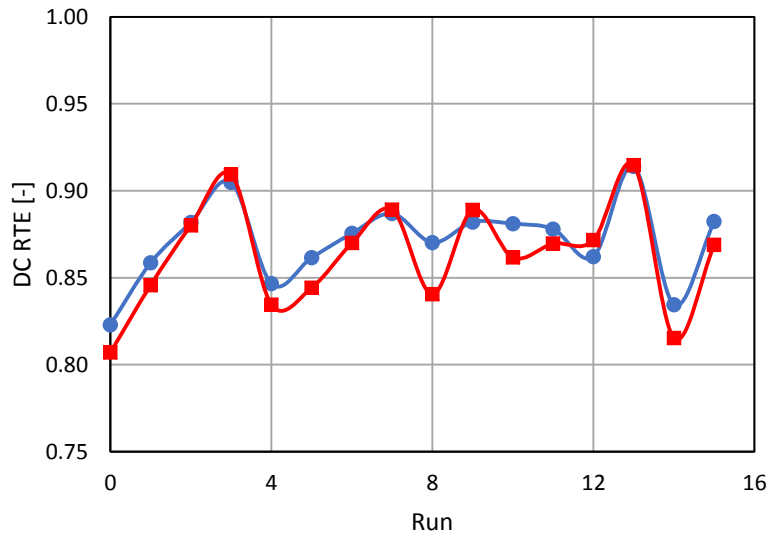


Figure 10. Measured (blue, circles) and predicted (red, squares) values by the models of Equation 11 and 12 on the data of the optimal characterisation experiment D for the DC efficiency (left) and the DC discharge capacity (right).

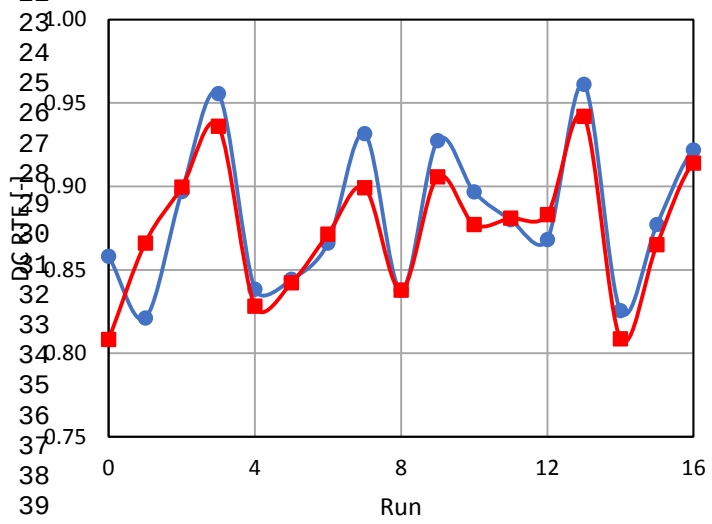
Reliable models should tell something about the general performance of the battery and should therefore also perform well on the data of other experiments, other than those that provide the data on which they are fitted. The models, fitted on the data from the optimal characterisation experiment, are therefore applied to the data of three previously conducted experiments which follow Design A. They are denoted as A.1, A.2 and A.3. Finally, the models are also tested on the data of an experiment following Design C, which was also conducted on the single RFB setup. Figure 11 displays the measured values of the experiments in blue circles, and the values which were predicted by the model from the optimal characterisation experiment in red squares.



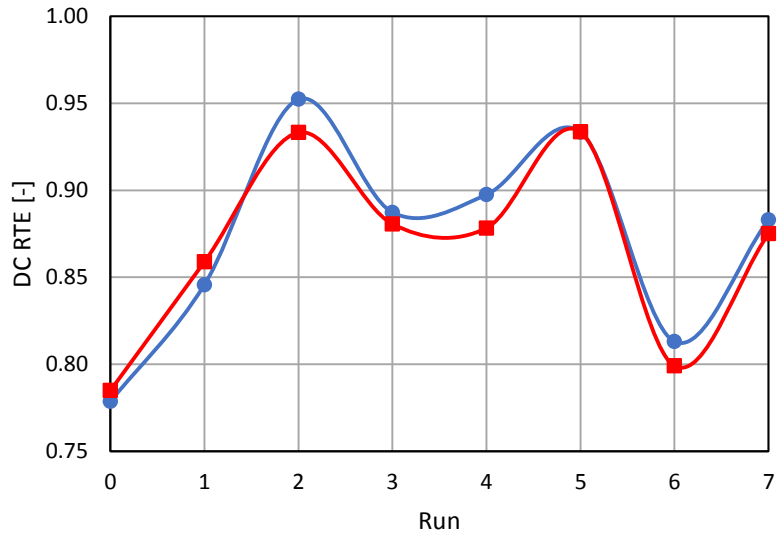
Experiment A.1



Experiment A.2



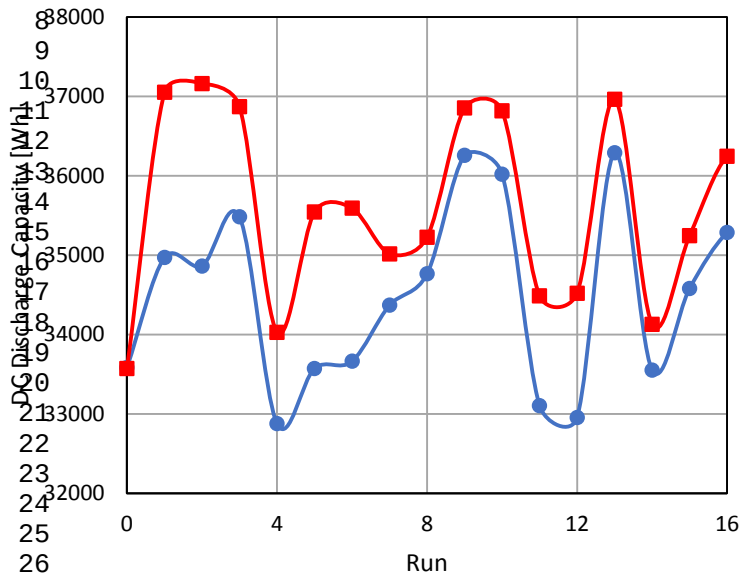
Experiment A.3



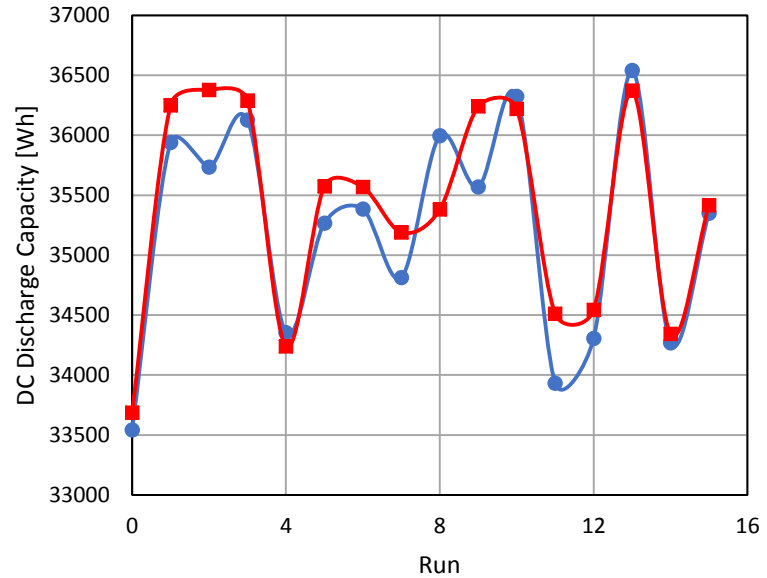
Experiment C

Figure 11. Measured (blue, circles) and predicted (red, squares) values by the DC efficiency model obtained from experiment D, applied to the data of earlier experiments.

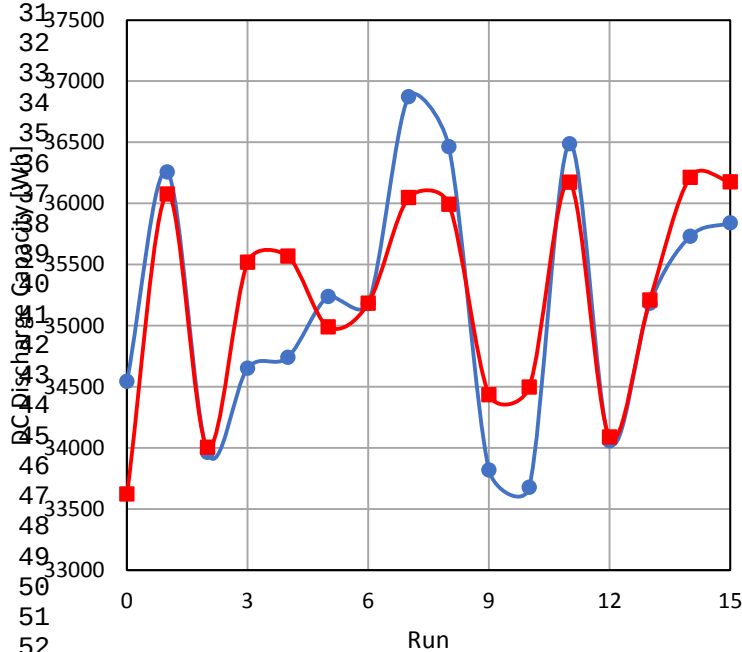
Likewise, Figure 12 displays the DC discharge capacity model which was fitted on the data from the optimal characterisation experiment. As in Figure 10, the model is applied to the data of three experiments following Design A (denoted as A.1, A.2 and A.3) and one experiment following Design C. The measured values are displayed in blue circles, and the predicted values are displayed in red squares.



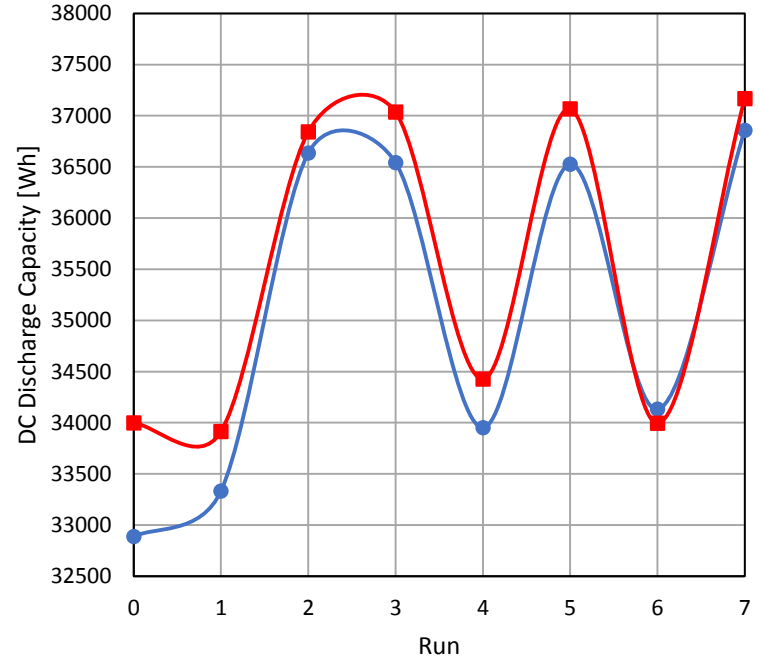
Experiment A.1



Experiment A.2



Experiment A.3



Experiment C

Figure 12. Measured (blue, circles) and predicted (red, squares) values by the DC discharge capacity model obtained from experiment D, applied to the data of earlier experiments.

These graphs demonstrate that the obtained models can be considered to be generally reliable, which is also expressed through the R^2 and RMSE values of the models on the data of earlier experiments. The statistically designed characterisation experiment therefore considerably outperforms the standard characterisation protocol in the sense that comprehensive and reliable battery performance information can be obtained from an experiment that is significantly shorter.

To indicate how powerful the designed characterisation experiment is compared to the standard protocol, Figure 12 demonstrates that the polynomial models, obtained from Experiment D (which only takes half the amount of time of standard characterisation), can reliably predict the performance of the RFB for the operating points that are classically evaluated during standard characterisation.

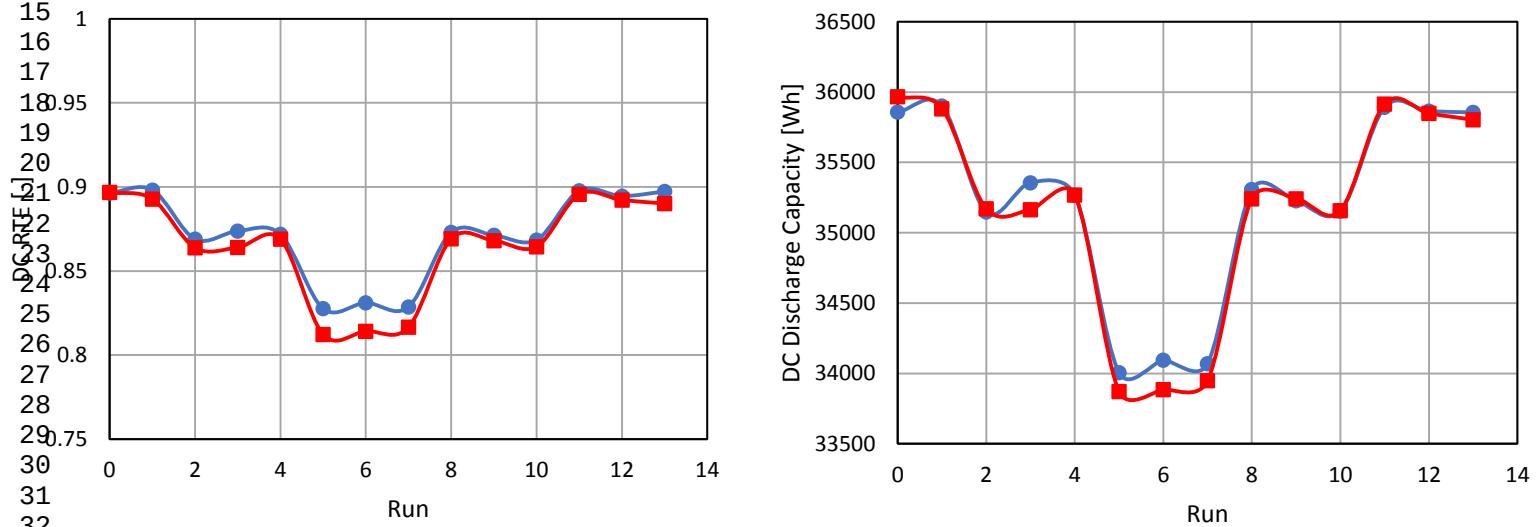


Figure 12 Measured values (blue, circles) of the standard characterisation experiment and predicted values (red, squares) by the polynomial DoE models, obtained from the orthogonal characterisation experiment.

4. Conclusion

Design of experiments has proven to be a reliable and appropriate tool to increase the efficiency and the quality of RFB characterisation experiments. It was shown that battery performance parameters (DC RTE and DC discharge capacity) could be reliably modeled by using only controllable RFB parameters (available to RFB end-users) and the electrolyte temperature. The electrolyte temperature was found to be a highly significant term in the models.

By identifying the parameters which are most influential for the DC RTE and the DC discharge capacity, appropriate RFB performance models could be formulated. This in turn facilitated the design of an optimal characterisation experiment. Identification of the dominant parameters in the system is time consuming but is likely only needed once for every RFB chemistry.

The optimal characterisation experiment results in empirical models for the DC RTE and the DC discharge capacity, which are able to predict RFB performance values for every setting that is within the model ranges. Therefore, the optimised characterisation experiment yields far more useful and comprehensive information than classical characterisation experiments, which only yield performance information for three operating points. Not only does the optimal characterisation experiment yield better information, it also takes a significantly shorter amount of time to conduct. Through DoE, the characterisation time for the 30 kWh UET Reflex module could be reduced from close to 13 days to 6.5 days.

The same principles can be applied to longer duration modules, for which DoE can reduce considerable characterisation times as well. DoE therefore proves its value as an efficient and reliable characterisation tool and considerably outperforms traditional characterisation procedures. As such, the use of DoE can accelerate the implementation and integration of RFBs wherever they can be used.

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A comprehensive and time efficient characterisation of redox flow batteries through Design of Experiments

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Abstract

As the need for a sustainable economy rightly drives the share of renewable energy, electric grids and supporting infrastructure must flexibly adapt. As valuable building blocks in integrated systems, battery energy storage systems (BESSs) can provide the required flexibility for energy and power applications. Redox flow batteries (RFBs) are emerging as promising alternatives to lithium-ion batteries to meet this growing demand. As end-users, RFB operators must characterise the batteries to learn more about the battery's behaviour and performance and better integrate such RFB technology into energy systems. Characterisation experiments yield this information, which is essential to successfully operate and integrate redox flow battery systems. However, conducting classical characterisation protocols can take more than two weeks for large RFB modules (capacities > 30 kWh), which is too long for an efficient RFB roll-out. Better characterisation methods are required to efficiently scale up, integrate and operate RFBs in an appropriate manner. Ideally, characterisation experiments would yield a more comprehensive understanding about the battery performance and behaviour in a shorter amount of time. In order to achieve this, statistical design of experiments (DoE) is explored as an RFB characterisation tool. DoE is a statistical method that makes optimal use of the available time and resources and increases the efficiency of experiments in a statistically sound manner. Designed experiments result in empirical models for the studied system, which can predict system outputs for a vast amount of operating points. This will enable optimal operation of the battery in terms of remaining capacity management and overall electrical efficiency. Through a number of such designed experiments, dominant RFB system variables could be identified, which allow reliable modelling of the RFB performance for different charge-discharge cycles. This facilitated the design of an optimised characterisation experiment. A 50% reduction of the required RFB characterisation time is achieved and the optimal experiment yields comprehensive information about the battery performance and behaviour. As such, a shorter and better RFB characterisation procedure is realised through DoE.

Keywords

Energy Storage, Redox Flow Battery (RFB), Design of Experiments (DoE), Characterisation, Energy Efficiency, Energy Management

1. Introduction

As the energy market is rightly transforming to become sustainable, the share of variable renewable energy is rapidly increasing. This comes with greater variations and unpredictability, which raises the need for flexibility in electric grids and supporting infrastructure [1] [2]. Scaling up stationary energy storage capacity is essential to enable the energy transition. Batteries are particularly suitable to play a crucial role in providing this flexibility, both for energy applications (e.g. time-shifting and peak shaving) and power applications (e.g. as frequency containment reserve) [3] [4].

Commented [OD1]: The abstract was rewritten to better convey the challenge we address, and why DoE is used to address it. The text is also adapted to better reflect our position as RFB end-user.

While a great share of industrial and research focus is on Lithium-ion batteries, redox flow batteries (RFBs) are emerging as promising alternatives. As opposed to Li-ion batteries and other chemistries, active species for the RFB redox reactions are stored in the electrolytes.

The RFB working principle (schematically displayed in Figure 1) thus makes it possible to independently scale energy capacity and power of the battery, which is beneficial for its flexibility. Fast response time and power capabilities also allow redox flow batteries to be operated as frequency containment reserve (FCR). With lifetimes potentially exceeding 20 years, greater recyclability and no need for cobalt or lithium, the batteries are more sustainable than their Li-ion counterparts, as recently shown in a detailed Life Cycle Assessment study comparing both battery types [5].

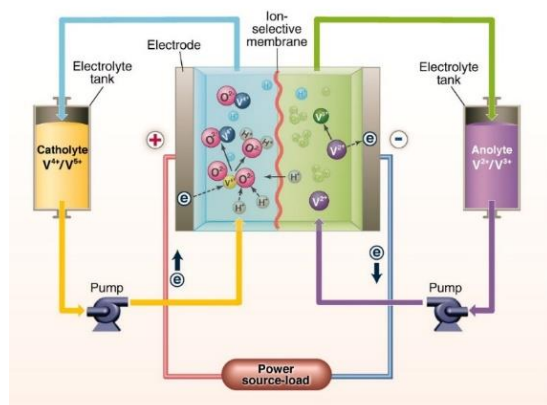


Figure 1. Redox flow battery working principle. Two half-cells circulate an electrolyte in which the active species are stored. During operation, ions migrate from one electrolyte to the other through an ion-selective membrane. This process is electrically matched by the movement of electrons through an external circuit. [6]

RFB end-users need a profound understanding of individual RFB behaviour to efficiently size, validate, integrate and operate the batteries with other systems. RFBs are therefore subjected to characterisation experiments to gain insights beyond specification sheet information. Classical characterisation procedures are essentially composed of a large number of charge-discharge cycles for which battery capacity and round trip efficiency (RTE) are measured and focus mainly on repeatability of the results. Conducting these protocols for the 30 kWh vanadium redox flow batteries (VRFBs) used in this work takes 311 hours, which is close to 13 days. The testing sequence essentially reveals the battery's RTE and full DC discharge capacity for three power ratings (nominal charge/discharge power, 2/3 nominal power and 1/2 nominal power).

While this information is indispensable, characterisation experiments should ideally yield more comprehensive information, which can be used in energy management systems (EMSs). Moreover, as longer duration batteries are needed to meet system requirements, conducting classical characterisation experiments becomes a tedious and time-consuming task since they involve repeated cycling over the full capacity range. Standard characterisation thus requires too much time for too little information, and presents a significant hurdle on the way to a more widespread and efficient implementation of RFBs.

Commented [OD2]: Our point of view as RFB end users is clarified through editing this paragraph.

To scale up RFB storage capacity and to efficiently integrate it into larger energy systems, there is a growing need for more time and resource-efficient characterisation experiments, especially if different use cases and possible value streams are covered with the same battery technology. Design of experiments (DoE) is therefore considered as a battery characterisation tool. DoE is a statistical technique which seeks to make optimal use of the available time and resources for experiments in general. Applying DoE to characterisation experiments would thus reduce characterisation times to a minimum, whilst obtaining the necessary information.

The data from designed experiments are used to fit empirical models which are continuous in the identified input parameters thanks to the multivariate approach. One feature of these models is that they can approximately predict system outputs (e.g. efficiency) for settings that have not been explicitly tested. In this regard, designed experiments, applied to RFBs, should outperform classical characterisation experiments, which only yield information about a limited number of operating points.

Whilst being widespread in chemical and pharmaceutical research, DoE seems to be only at the start of its potential for battery R&D, and it has only been applied to Li-ion batteries so far. For Li-ion batteries, designed experiments have been used to obtain better models, better performance and better battery designs.

Pozzi et al. [7] used designed experiments to efficiently obtain the parameters for an isothermal single particle model with electrolyte dynamics (SPMe). Su et al. [8] used designed experiments to identify the most influential stress factors affecting the cyclic ageing process in Li-ion batteries. Mathieu et al. [9] successfully used D-optimal experiments to fit a semi-empirical model derived from a polynomial approximation of a physical ageing model, which took both calendar and cyclic ageing into account. Baghdadi et al. [10] used a similar approach and further optimised it.

Boadu et al. [11] optimised the parameters for pulse-charging a lithium-polymer (LiPo) battery using design of experiments. Liu and Luo [12] similarly used designed experiments to optimise a multistage constant current (MSCC) charging method. Ryne et al. [13], Dong et al. [14] and Kim et al. [15] used DoE approaches to optimise the physical and chemical design of lithium-ion battery systems, yielding improved capacities, improved energy densities, and reduced polarisation. Lombardo et al. [16] confirm the potential of DoE for manufacturing and optimisation but are sceptical about the application range of the method. Finally, Panda et al. [17] regard DoE as “a fascinating and amazingly useful tool to enhance any study which deals with various parameters by a minimum number of experiments [...]” and consider it remarkable that experimental design is used so little in academia [17].

While DoE has yielded good results in the above mentioned works, it has not been used for redox flow batteries so far. This study is therefore the first to explore DoE for RFBs and aims to establish it as a reliable and efficient RFB characterisation tool. The main goal is to design a characterisation experiment that yields comprehensive battery information in a minimum amount of time. To this aim, this work evaluates whether or not RFB performance can be reliably modelled with a limited set of factors through DoE. DoE input and output parameters are identified based on the most relevant RFB parameters and the degree to which they can be varied by end-users. The battery itself is not modified during the experiments, only the operational parameters which are controllable by end-users. Through screening experiments, DoE is used to test the influence of these parameters and to identify the dominant parameters in the system. When the most influential parameters are identified, an appropriate and optimal characterisation can be designed. In order to validate the obtained models, their performance is evaluated on the data of the other experiments as well.

Commented [OD3]: The phrasing was adapted to be clearer and more straightforward. The role of DoE in this work is explained more clearly.

Commented [OD4]: References 16 and 17 were added. Both works appeared in recent months. These articles review several computational techniques and numerical approaches to battery systems. Li-ion batteries in particular.

Commented [OD5]: This paragraph was rewritten to bring more structure to the introduction. The text has been adapted to explain our aim and our approach in a clearer manner.

Section 2 discusses the utilised materials and methods. The experimental setup is explained and the DoE methodology is outlined. This section also details the application of DoE to RFBs, and provides an overview of the conducted experiments. Section 3 elaborates on the conducted experiments and their corresponding results. The experiments are grouped on the basis of their design. Finally Section 4 concludes with the main findings and a discussion of their implications.

2. Materials and methods

2.1 Setup

Two test setups are used. The first one consists of a single 7.5 kW – 30 kWh UET Reflex module connected to a 15 kW Victron Quattro power converter. During charging, the power converter converts 230 V AC from the grid to DC for the battery. Accordingly, the power converter converts DC from the battery to 230 V AC for the grid during discharging. The battery is controlled by an energy management system (EMS) in an external computer which also collects data from the measurements. The EMS sends power commands to the power converter and handles communication between the power converter and the battery.



Figure 2. Single RFB test setup. The battery is controlled by an energy management system in a computer, which also handles communication between the inverter (blue box) and the battery. Aside from this, the computer also collects measurements via the battery management system, which is located at the top of the RFB module.

The second setup features a string of 3 UET Reflex modules, connected in series. The modules are linked to a 90 kW Triphase power converter. The Triphase power converter is more efficient and has a faster response time compared to the power converter in the single-unit setup.



Figure 3. Series RFB test setup. Three UET RFBs are connected in series and form a string of batteries, which facilitates operation at greater voltages. The series setup has a nominal voltage of 144V and a maximum voltage of 192V.

2.2 Methodology – Design of experiments

In order to apply the DoE method, the studied system is viewed as a process with corresponding inputs and outputs. A number of controllable parameters ($x_1, x_2, \dots, x_p$) and a number of uncontrollable parameters ($z_1, z_2, \dots, z_q$) are identified in order to study their influence on the system response y . This system view is visualised in Figure 4. The selection of the controllable and uncontrollable parameters is usually based on a preliminary understanding of the system. Experimenters must be able to change the values of the controllable parameters between consecutive measurements of the system response y . Designing experiments then consists of selecting the combinations of levels for the controllable parameters ($x_1, x_2, \dots, x_p$) at which the response y must be measured. Each experiment consists of a number of tests at different combinations of levels for ($x_1, x_2, \dots, x_p$). With these measurements, an empirical model is fitted that expresses y as a polynomial function of ($x_1, x_2, \dots, x_p$) [18].

Commented [OD6]: This text was thoroughly reviewed to explain the DoE working method more clearly and more concisely. This brings more structure to the text and Section 2 in particular.

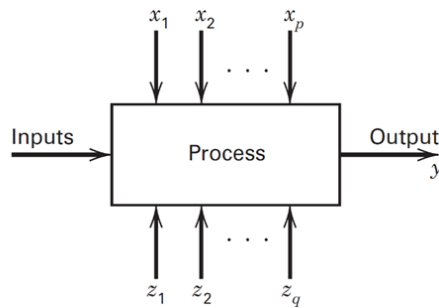


Figure 4. DoE system view. System parameters are divided in different groups. The inputs are characterised by a number of controllable parameters ($x_1, x_2, \dots, x_p$). Their effect is studied on the system outputs, which are also affected by a number of uncontrollable parameters ($z_1, z_2, \dots, z_q$). [18]

The general applicability of the method is based on the Pareto principle which proposes that any real process is mostly driven by a limited amount of important factors and Taylor's theorem which states that any function $Y = f(x_1, x_2, \dots, x_p)$ can be approached by a polynomial of first, second, ... order in an area that is sufficiently small [19].

In order to select appropriate levels for the controllable factors at which the response must be measured, an a priori model must be proposed. The selection of an adequate expression is not straightforward but can rely on two principles: the Pareto principle (or sparsity-of-effects) and hierarchy. Hierarchy entails that the variability caused by first order effects exceeds the variability that is caused by second order effects. Similarly, second order effects will have a greater influence on the system response than third order effects, and so on. This implies that before expanding the model with third order terms, second order terms should already be included [19]. These two principles (sparsity-of-effects and hierarchy) were verified and validated by Li et al. [20], who documented a meta-analysis of 113 datasets from published factorial experiments.

Once an a priori model has been proposed, which expresses an output parameter y as function of input parameters ($x_1, x_2, \dots, x_p$), the experiment can be designed according to different optimality criteria. The selected optimality criterion imposes a number of requirements on the values of ($x_1, x_2, \dots, x_p$) in the experiment, such that the resulting data provide the required information or answer the relevant questions. In this work, the D-optimality, I-optimality and orthogonality are used. D-optimality is used in order to identify the dominant parameters in the system. I-optimality is used to optimise the model predictions. Finally, orthogonality is used in order to obtain precise model parameter estimations which are mutually independent. Once the measurements of the tests have been collected, the proposed models are fitted with ordinary least squares or stepwise regression [19] [21].

The design of the experiments and the analysis of the resulting data are carried out in JMP. JMP is statistical software developed by SAS and is considered to be an excellent program by leading statisticians. A custom design platform takes into account potential resource limitations and the difficulty to change factors [18] [19]. The program puts a lot of emphasis on graphics and interactivity. This makes it easier to analyse the data and draw conclusions from it [22] [23]

Commented [OD7]: Figure 4 was originally a part of what is now Figure 6. We believe that the current order, in which the figures have been separated, better visualises the system view that is explained in Section 2.2 and therefore provides a clearer explanation leading up to the application of this system view to RFBs in Figure 6.

The reference to the original work explaining this figure was also added in the figure description.

Commented [OD8]: The explanation of the a priori models under Section 3, Design A now explicitly refers to the methods section. This way, it is clearer how the method is applied.

Commented [OD9]: The importance of the optimality criterion and its selection was not sufficiently explained and stressed in the original version of the manuscript. Therefore the link between the models and the experiments was not clear. This paragraph has therefore been extended and the phrasing was improved to better explain how the experiments are designed, based on the models. As such, a more structured explanation is provided for our approach and our working method.

2.3 DoE battery system view

The designed RFB experiments consist of a number of charge-discharge cycles for which the controllable RFB parameters are varied and for which the battery performance parameters are measured. In the experiments, each battery charge-discharge cycle is considered to be an experimental test or “run” with corresponding inputs and outputs. Many parameters have an influence on the RFB’s performance, but not all of them can be controlled by RFB end-users and operators. Table 1 provides an overview of the studied RFB parameters that may influence the battery performance, and details how they are measured or controlled. For the parameters that can be varied by RFB end-users, the lower limit and upper limit, as used in this work, are included.

Commented [OD10]: This section was completely rewritten following the review. Through the feedback we received, we realised that the selection and the availability of the parameters which were used in the DoE was not clearly reflected in the original manuscript. Therefore, Section 2.3 now includes a better and more comprehensive explanation of the parameters that are available to us as end users, and which of those parameters we can control for use in the DoE.

Table 1. RFB parameters that may affect performance

Parameter	Measurement	Controllable by operator	Lower limit	Upper limit	Comments
Minimum state of charge (SOC)	Via open circuit voltage (OCV*)	Yes	0%	37%	Controlled through battery management system (BMS)
Maximum SOC	OCV	Yes	75%	100%	Controlled through BMS
Charge rate	N/A	Yes	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$	Controlled through BMS P_{nom} refers to the nominal RFB power, which is 7.5 kW
Discharge rate	N/A	Yes	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$	Controlled through BMS
Resting time at minimum SOC	N/A	Yes	15 min	720 min	Controlled through BMS
Resting time at maximum SOC	N/A	Yes	15 min	720 min	Controlled through BMS
Electrolyte temperature	Temperature sensor at catholyte and anolyte	No	N/A	N/A	-
Ambient temperature	Temperature sensor at top cover	No	N/A	N/A	-
Ageing and degradation	Via state of health (SOH)	No	N/A	N/A	Apart from measurements, SOH is also indicated by capacity and efficiency values
Electrolyte flow	N/A	No	N/A	N/A	Controlled through circulation pump
Electrolyte composition	N/A	No	N/A	N/A	Concentration of different compounds

Commented [OD11]: Table 1 was added to provide more clarity regarding the availability, the controllability, the measurements and the used limits of the RFB parameters.

*The UET Reflex RFB contains a reference cell through which small amounts of both electrolytes are circulated. The electrolytes remain separated, although not by an active exchange membrane. The OCV of the battery can be measured in this cell at all times. The OCV measurements are automatically compared with the SOC versus OCV curve, which is a one-on-one relationship provided by the RFB manufacturer.

Commented [OD12]: This remark was added to clarify how the OCV is measured and how the SOC can be determined based on this information.

Operators can set the values for the controllable parameters through the battery management system (BMS), which is the electronic system that controls the module, monitors critical parameters, protects the module from abnormal conditions and interfaces with higher level control.

Figure 5. schematically displays the nomenclature of the controllable parameters on two consecutive charge-discharge cycles. Note that the values of these parameters can be chosen and varied for each cycle by battery operators.

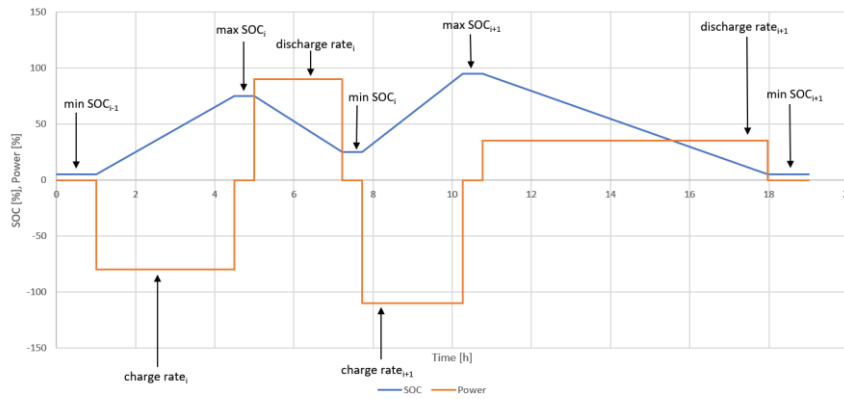


Figure 5. Charge and discharge rates (orange) and corresponding SOC variation (blue) for two consecutive charge-discharge cycles in a designed experiment.

Various parameters influence battery performance, but not all of these parameters can be controlled by RFB operators. As such, their values can not be actively altered between consecutive experimental runs, which makes it impossible to include them in the design of the experiments. Other parameters do not vary considerably throughout the experiment. As a consequence, it does not make sense to include them in the models either since their values do not vary in a range that is large enough to reliably model them. The only exception to this is the electrolyte temperature, which varies in a considerable window throughout the measurements. Its effect on the battery performance is discussed in Section 3, under Designs A and C.

The studied RFB output parameters are the corrected DC discharge capacity and the DC RTE, calculated with corrected charge and discharge capacities. As a result of actively varying minimum SOC and maximum SOC values, the charge and discharge capacities change between consecutive cycles. Therefore, in order to compare battery performance for different cycles, the charge and discharge capacities are scaled such that the corrected capacities correspond to complete charge-discharge cycles (SOC: 0 → 100% → 0). Based on the corrected DC capacities, the corresponding DC RTE for a cycle i is defined as:

$$\eta_{DC,i} = \frac{\text{Scaled DC discharge capacity}_i}{\text{Scaled DC charge capacity}_i} \quad (1)$$

The DC RTE can vary between 0 and 1. Note that the auxiliary power required to feed the pumps of the RFB (500 W) is implicitly excluded from the efficiency calculation. The pumps also keep circulating the electrolyte while the battery is at rest. Note that this is a manufacturing decision and therefore outside the control of RFB end-users.

Commented [OD13]: The original manuscript was not clear about the purpose and the parameters of Figure 5. This has now been addressed through the addition of Table 1 and the changes to the text.

When the system view of Figure 4 is applied to the UET Reflex module (the RFB under study), Figure 6 is obtained by using the parameters from Table 1.

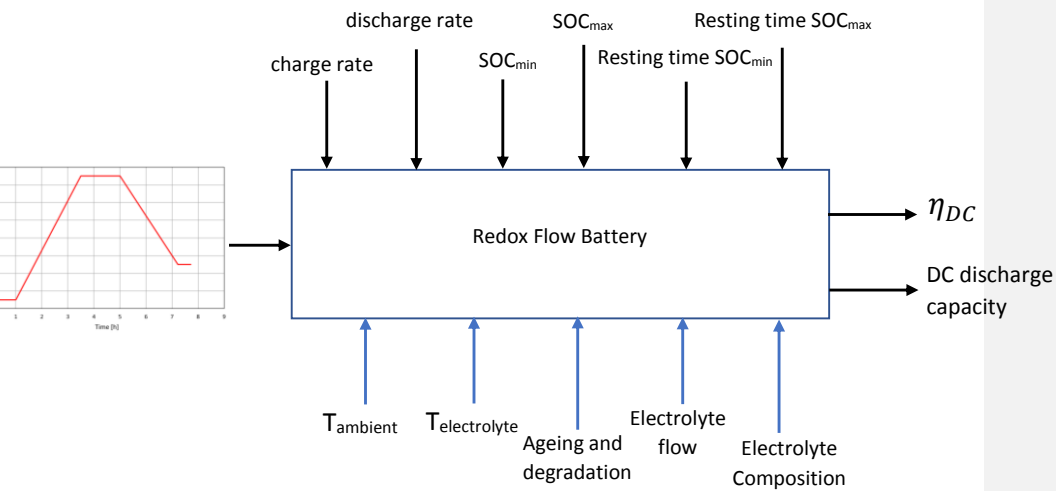


Figure 6. Redox flow battery system view. System parameters are divided in different groups. The inputs (left of the box) translate to charge-discharge cycles for the RFB, which are characterised by a number of controllable parameters (on top of the box). Their effect is studied on the system outputs (right of the box) which are also likely affected by a number of uncontrollable parameters (below the box).

Commented [OD14]: Figure 6 has been updated to be consistent with Table 1.

2.4 Overview of the experiments

Table 2 provides an overview of the designed experiments that were performed and their corresponding durations, with the ranges of the parameters that are varied between the cycles. The design of the experiments is explained in Section 3. Design 0 is not designed with DoE but denotes the characterisation experiment corresponding to the standard protocol. It is briefly discussed in the next section to facilitate comparison with the designed experiments.

Table 2. Overview of the designed experiments

Design	Setup	Design criterion	Duration [h]	Parameters	Lower limit	Upper limit
0	Single UET	Standard protocol	311	Power rating	$0.5 \cdot P_{nom}$	P_{nom}
A	Single UET	D-optimality	204	Charge rate	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$
				Discharge rate	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$
				Minimum SOC	0%	25%
				Maximum SOC	75%	100%
B	Series UET	D-optimality (16 runs)	260	Charge rate	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$
				Discharge rate	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$
		D+I-optimality (27 runs total)	370	Minimum SOC	5%	37%
				Maximum SOC	75%	95%
C	Single UET	D-optimality	476	Charge rate	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$
				Discharge rate	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$
				Minimum SOC	5%	25%
				Maximum SOC	75%	95%
				Resting time	0.5 h	12 h
				Maximum SOC	0.5 h	12 h
D	Single UET	Orthogonality	155	Charge rate	$0.5 \cdot P_{nom}$	$1.1 \cdot P_{nom}$
				Discharge rate	$0.5 \cdot P_{nom}$	$0.9 \cdot P_{nom}$
				Minimum SOC	0%	37%
				Resting time	0.5 h	4 h

Commented [OD15]: This section was originally a part of Section 2.3 but has been separated in order to bring more structure to the article.

3. Results and discussion

Experiment 0

Experiment 0 denotes the classical characterisation experiment which follows the standard characterisation protocol. This experiment essentially reveals the battery's RTE and full discharge capacity for three power settings (nominal charge/discharge power, 2/3 nominal power and 1/2 nominal power), which are equal for charging and discharging. Conducting standard characterisation protocols for the 7.5 kW – 30 kWh UET Reflex modules takes 311 hours, which is close to 13 days.

The standard characterisation revealed that the UET Reflex modules considerably outperform their specification sheet values, both in terms of DC RTE and DC discharge capacity. While the specification sheet DC RTE and DC discharge capacity are reported to be 80% and 30 kWh at nominal power respectively, measurements up to 82% and 34 kWh for these respective parameters were obtained.

Designed experiments

Through 7 experiments conducted on the single RFB module and 3 experiments conducted on the string of RFB modules connected in series, the dominating factors affecting the battery performance could be identified and confirmed. Once these most influential parameters were identified, appropriate model expressions for the DC RTE and DC discharge capacity could be formulated. These expressions facilitated the design of an optimal characterisation experiment, which outperforms standard characterisation protocols both in terms of experimentation time and in terms of the quality of the resulting information. The experiments are discussed in groups. Sections A, B, C and D each discuss a number of experiments which follow a similar design or reasoning.

Design A

The first four experiments were conducted on the single RFB module following a D-optimal design scheme. They are meant to identify the most influential controllable parameters in the system. The D-optimality criterion is used since it is ideal for screening experiments, which are used to identify the dominant factors in a system. Moreover, D-optimality maximises the information gained from the experiment [19] [21]. An elaborate explanation about the mathematical background of this approach, based on the Fisher information matrix has been published by Fedorov 1972 [24].

The experiments were designed to fit and test the a priori models displayed in Equations 2 and 3, which include four of the six controllable parameters of Table 1. The models only include controllable parameters for the reasons detailed in Section 2.3. Designing an experiment based on a model requires selecting the settings for the system parameters at which the response must be measured. This is not possible for uncontrollable parameters, of which the settings can not be controlled. The resting times at minimum and maximum SOC are not included in these models because they were thought to be insignificant at this stage. The experiments of Design C (below) have refuted this assumption however.

$$\begin{aligned}\eta_{DC} = & \beta_{\eta,0} + \beta_{\eta,1}CR + \beta_{\eta,2}DCR + \beta_{\eta,3}SOC_{\max} + \beta_{\eta,4}SOC_{\min} + \beta_{\eta,5}CR \cdot DCR \\ & + \beta_{\eta,6}CR \cdot SOC_{\max} + \beta_{\eta,7}CR \cdot SOC_{\min} + \beta_{\eta,8}DCR \cdot SOC_{\max} \\ & + \beta_{\eta,9}DCR \cdot SOC_{\min} + \beta_{\eta,10}SOC_{\max} \cdot SOC_{\min} + \beta_{\eta,11}CR^2 + \beta_{\eta,12}DCR^2 \\ & + \beta_{\eta,13}SOC_{\max}^2 + \beta_{\eta,14}SOC_{\min}^2 \quad (2)\end{aligned}$$

Commented [OD16]: The explanation of the designed experiments was adapted to convey our approach in a clearer and more concise manner.

$$\begin{aligned}
\text{DC Discharge Cap.} = & \beta_{\text{cap},0} + \beta_{\text{cap},1}\text{CR} + \beta_{\text{cap},2}\text{DCR} + \beta_{\text{cap},3}\text{SOC}_{\text{max}} \\
& + \beta_{\text{cap},4}\text{SOC}_{\text{min}} + \beta_{\text{cap},5}\text{CR}\cdot\text{DCR} + \beta_{\text{cap},6}\text{CR}\cdot\text{SOC}_{\text{max}} \\
& + \beta_{\text{cap},7}\text{CR}\cdot\text{SOC}_{\text{min}} + \beta_{\text{cap},8}\text{DCR}\cdot\text{SOC}_{\text{max}} + \beta_{\text{cap},9}\text{DCR}\cdot\text{SOC}_{\text{min}} \\
& + \beta_{\text{cap},10}\text{SOC}_{\text{max}}\cdot\text{SOC}_{\text{min}} + \beta_{\text{cap},11}\text{CR}^2 + \beta_{\text{cap},12}\text{DCR}^2 \\
& + \beta_{\text{cap},13}\text{SOC}_{\text{max}}^2 + \beta_{\text{cap},14}\text{SOC}_{\text{min}}^2 \quad (3)
\end{aligned}$$

In the models, the charge rate, the discharge rate, the minimum SOC and the maximum SOC are denoted as CR, DCR, SOC_{min} and SOC_{max}, respectively. The β 's represent the model parameters that need to be estimated with the experimental data. The models are structured such that they include an intercept (β_0), first order terms and second order terms (two-factor interactions ($x_i \cdot x_j$) and quadratic effects (x_i^2)). As such, the a priori models are based on the sparsity-of-effects and hierarchy principles discussed in Section 2.2. The sparsity principle is applied by only including the few controllable factors which are likely to exert a significant influence on the RFB performance. Hierarchy is respected such that only the first and second order terms of the selected parameters are included, which will cause greater variability than higher order terms of the same parameters. If the second order terms are found to be highly significant, the model will be expanded with third order terms.

To gain insight into the relative importance of the factors, they are ranked on the basis of their corresponding p -values. In order to define the p -value, consider the test statistic β_i (a model coefficient) and a null hypothesis stating $\beta_i = 0$. The p -value is then defined as "the probability of obtaining a value for the test statistic that is as extreme or more extreme than the value actually observed." [25] The probability is calculated under the null hypothesis. The lower the p -value, the lower the probability that the observed parameter value would be obtained under the null hypothesis. This means that there is a lower chance of the null hypothesis being true and thus a higher chance of β_i differing from 0. This in turn implies that the factor has a higher likelihood of actually being significant in the system. Factors for which the p -value is lower than 0.05 are considered to be significant. This is common practice in statistics [19].

Insignificant factors are excluded as much as possible in order to get compact, reliable models. If the quadratic term of a factor turns out to be significant however, the corresponding linear term is also included in the model, following the hierarchy principle.

For the DC RTE, the statistically dominant effects turned out to be the discharge rate, the charge rate and the electrolyte temperature. Although the electrolyte temperature is not a controllable factor, it is easy to measure and the experiments demonstrated that including a temperature term in the models can significantly improve their prediction capabilities. This requires that the electrolyte temperature varies sufficiently throughout the measurements. The ranking of the effects on the basis of their corresponding p -values is displayed in Figure 7.

Commented [OD17]: The explanation regarding our choice of a priori models has been rewritten. The new text elaborately explains and justifies the proposed starting models with better references to the updated paragraphs of Section 2 and DoE principles in general.

Commented [OD18]: We elaborated on the definition of the p -value and have provided a complete yet concise explanation of the concept. The decision to use a cut-off value of 0.05 for p -values is based on common practice in statistics.

Commented [OD19]: The phrasing in these paragraphs was adapted to provide a better explanation for the terms that were excluded from the original models. As such, our approach is conveyed in a more structured manner. The text now better details how the experiments, designed with the models from Equations 2 and 3, finally resulted in the models in Equations 7 and 10, respectively, by excluding the insignificant terms.

Effect Summary				
Source	LogWorth			PValue
discharge rate(50,90)	6,356			0,00000
charge rate(50,110)	4,791			0,00002
Temperature	3,780			0,00017

Figure 7. Dominant effects affecting the DC RTE in the first experiments, following Design A.

No significant two-factor interactions ($x_i \cdot x_j$) or quadratic effects (x_i^2) were detected, and the minimum and maximum SOC of the cycle seemed to be of lesser importance.

In the scope of this work, only quantitative continuous factors are included in the models. Since these system inputs vary in different ranges, estimates of the model coefficients can vary greatly. Coding the factors makes it possible to see the relative importance of the effects at first glance. As an example, the coding for the charge rate term in the model is given. If a factor varies between a lower end point L and an upper end point U , the interval $[L, U]$, or [50%, 110%] for the charge rate, is transformed to $[-1, +1]$ according to:

$$M = \frac{L + U}{2} = \frac{50 + 110}{2} \quad (4)$$

$$\Delta = \frac{U - L}{2} = \frac{110 - 50}{2} \quad (5)$$

$$x_k = \frac{l_k - M}{\Delta} = \frac{l_k - 80}{30} \quad (6)$$

Here, M is the midpoint of the original interval and Δ represents half of its range. In scaled values, x_k will vary linearly between its low level -1, corresponding to the original L , and its high level +1, corresponding to the original U [19]. This leads to the following model for the RTE, which is fitted with ordinary least squares and expressed with coded terms:

$$\eta_{DC} = 0.77487 - 0.014986 \left(\frac{CR - 80}{30} \right) - 0.020247 \left(\frac{DCR - 70}{20} \right) + 0.0029175 \cdot T \quad (7)$$

The quality of the obtained models is evaluated by using the coefficient of determination R^2 and the root mean square error RMSE.

The coefficient of determination R^2 is the fraction of the variation in the data that can be explained by the obtained regression model. It is calculated by comparing the regression sum of squares SSR with the total sum of squares SSTO in the data. The regression sum of squares can also be written as one minus the error sum of squares SSE, as denoted in the following equation:

$$R^2 = \frac{SSR}{SSTO} = 1 - \frac{SSE}{SSTO} = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (8)$$

In this expression, $\hat{y}_i$ represents the prediction of the model for measurement y_i and $\bar{y}$ represents the average value of the measurements. For a perfect model, there are no errors on the predictions and the R^2 equals one. Note that R^2 can even be negative, indicating that the sum of squared errors is larger than the total sum of squares, and the model yields worse predictions than a horizontal line on the average response [21].

Finally the root mean square error RMSE is used to indicate how far the predictions are off on average. It serves as an estimation of the standard error on the predictions of the actual observations [18].

$$\text{RMSE} = \sqrt{\sum_{i=1}^n \frac{(\hat{y}_i - y_i)^2}{n}} \quad (9)$$

The model performance was also evaluated by applying the models to the data of other experiments. Ideally, the R^2 and RMSE values calculated on a new dataset should be close to the R^2 and RMSE values for the dataset on which the model was originally fitted.

The R^2 and the RMSE of the efficiency model of equation (7) respectively amount to 0.934 and 0.00679. The R^2 indicates that 93.4% of the variation in the data can be explained by the model. Furthermore, the RMSE indicates that the predictions are only 0.679% off on average, which amounts to a 0.78% relative error compared to the average efficiency of the experiment.

For the DC discharge capacity, the following dominant effects were identified on the basis of their corresponding p -values: the discharge rate, the squared minimum SOC and the electrolyte temperature. The discharge capacity model is obtained accordingly:

$$\begin{aligned} \text{DC Discharge cap.} = & 41400.6 - 1262.1 \left(\frac{\text{DCR} - 70}{20} \right) - 140.31 \left(\frac{\text{SOC}_{\min} - 12.5}{12.5} \right) \\ & + 201.72 \left(\frac{\text{SOC}_{\min} - 12.5}{12.5} \right)^2 - 189.98 \cdot T \end{aligned} \quad (10)$$

With an R^2 of 0.957 and a RMSE of only 256 Wh, this model shows an excellent fit on the experimental data. Since the squared minimum SOC is statistically significant, its corresponding linear term is also included in the model despite being statistically insignificant. This way, the hierarchy principle is respected. No other quadratic effects or significant two-factor interactions were detected for the DC discharge capacity.

Design B

The experiments discussed in this section were executed on the series RFB setup and are designed with the same controllable parameters as experiment A. As a first experiment, a D-optimal design similar to Design A was conducted on the series RFB setup. Later, an I-optimal 8-run extension to the original experiment was conducted as a separate experiment. The I-optimal extension is added in order to study the potential improvement of the models. If it is fairly certain that an expression is appropriate to model a system, I-optimality can be used to optimise the prediction accuracy of the empirical model by minimising the variance of the predictions over the entire experimental region, relative to the variance of the statistical error on the model predictions, σ_e^2 [18] [19]. Finally, both (D- and I-optimal) designs were conducted as consecutive parts of one experiment, which is discussed below. The D-optimal part of the experiment took about 260 hours. The complete experiment took 370 hours.

Following the same procedure as discussed for Design A, a DC efficiency model is obtained. The significant parameters are the charge rate, the discharge rate, the minimum SOC and the maximum SOC. Likewise, the DC discharge capacity model is composed of terms for the charge rate, the discharge rate, the maximum SOC, the minimum SOC and quadratic terms for the maximum and the minimum SOC.

The data indicate that the change in R^2 due to the I-optimal extension is negligible but that a relative reduction of 17% and 8% of the RMSE is achieved for the DC RTE and the DC discharge capacity model, respectively.

Since the RMSE serves as estimator for the standard deviation on model predictions, an approximated probability distribution function (PDF) for the actual output values can be plotted based on its value. Figure 8 displays the effect of the reduced RMSE on the PDF for the actual output value, when the model predicts an output that corresponds to the mean of experiment B. The green lines correspond to the models fitted on the original D-optimal runs while the red lines correspond to the models fitted on the complete experiment.

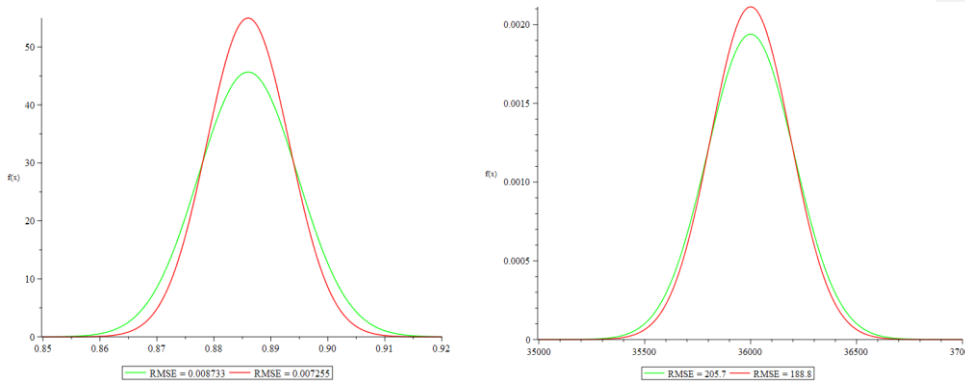


Figure 8. Small improvement of the added runs on the approximated probability distribution function of model predictions for the DC RTE (left) and the DC discharge capacity (right). The green lines correspond to the PDF of the models fitted on the original D-optimal runs. The red lines correspond to the models fitted on the complete experiment.

The improvement of the models due to the extra runs is limited, which is also visible in Figure 7. It is therefore concluded that the I-optimal extension to the original D-optimal experiment is not worth the extra experimentation time, which amounts to 110 hours.

Design C

While the models of experiment A include a significant temperature term, the capacity model of experiment B yielded good results without one. With the data so far, the influence of the electrolyte temperature on the RFB performance parameters is not clear. For batteries in general, the electrolyte temperature plays an important role. Since the temperature is not actively regulated for redox flow batteries, finding an appropriate way to quantify its influence on the battery performance is particularly important.

From a physical point of view, it makes sense that the electrolyte heats up faster when the battery operates at higher power ratings over large SOC ranges. Part of the temperature influence is thus indirectly quantified in the models already. To gain a better understanding of the temperature effect, resting times are varied in this experiment. This way, the electrolyte can cool off and the process can be quantified with controllable factors. The experiment is performed on the single RFB setup.

The resting times are varied between 15 and 720 minutes (12 hours). Since a redox flow battery has a considerable thermal inertia, the waiting times are varied over a large range in order to get a clear image of their effect on the RFB outputs. The resting time at minimum SOC for a cycle ($\text{Restingt}_{\text{SOC,min}}$) is defined as the time the battery remains at the minimum SOC of the previous cycle. This factor is meant to quantify the influence of the amount of time between subsequent cycles. The resting time at maximum SOC ($\text{Restingt}_{\text{SOC,max}}$) on the other hand is the amount of time between the charge and the discharge of a cycle. The parameters are schematically displayed in Figure 9. The experiment has a 16-run D-optimal design, which includes active variation of all six controllable parameters. As such, the experiment is meant to detect which of the controllable parameters have the most significant effect on the studied performance parameters.

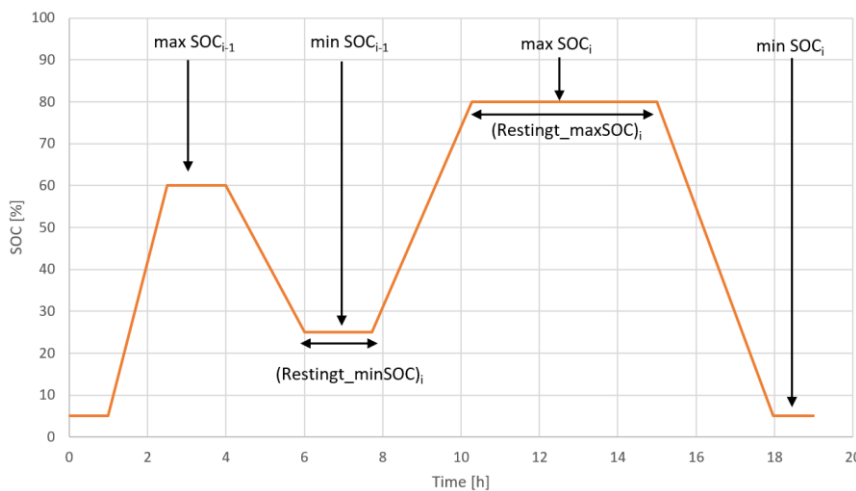


Figure 9. Definition of the resting times on the SOC curve for two consecutive charge-discharge cycles.

In this experiment, the resting time at maximum SOC was detected as a statistically significant parameter for predicting the DC efficiency and the DC discharge capacity. As discussed in Section 2.3, the pumps keep the electrolytes circulating, even when the battery is at rest. As such, the electrolytes are kept homogeneous throughout the experiment, also during rest. This may explain why the resting time at maximum SOC is found to be statistically significant. Following the same procedure as discussed for Design A, a DC efficiency model is obtained which includes terms for the charge rate, the discharge rate, the resting time at maximum SOC and the electrolyte temperature. This model attains an R^2 of 0.957 and an RMSE of 1.46% on the data of Experiment C.

Commented [OD20]: This paragraph was adapted to better justify our choice of the used optimality criterion. As such, the relation between the proposed model and the conducted experiment is better conveyed.

Commented [OD21]: Likewise, this paragraph was revised to better justify how the models are adapted following the results from the experiments, thereby bringing more structure to the results.

Likewise, the DC discharge capacity model features terms for the discharge rate, the resting time at maximum SOC and the electrolyte temperature. It yields an R^2 and an RMSE of 0.959 and 406 Wh respectively. Throughout the experiments, it became clear that a temperature term only provides added value to the models if the temperature range is considerable for the experiment (ideally it varies between the extremes of 20°C and 38°C). This implies that in order to fully capture the effect of the temperature on the DC RTE and the DC discharge capacity, the battery should not be operated for a number of days before the start of the characterisation experiment. This way, the electrolyte temperature can be close to ambient temperature at the start of the experiment, and can vary over a large range during the RFB characterisation.

Design D – The optimally designed characterisation experiment

With the insights from Designs A, B and C, the most influential controllable parameters were identified. Based on this selection, the following expressions are formulated, which can adequately model the RFB performance parameters with only a limited set of variables.

$$\eta_{DC} = \beta_{\eta,0} + \beta_{\eta,1} \left(\frac{CR - 80}{30} \right) + \beta_{\eta,2} \left(\frac{DCR - 70}{20} \right) + \beta_{\eta,3} \left(\frac{RT_{SOC_{max}} - 127.5}{112.5} \right) + \beta_{\eta,4} \left(\frac{SOC_{min} - 12.5}{12.5} \right) + \beta_{\eta,5} \cdot T \quad (11)$$

$$DC \text{ Discharge Cap.} = \beta_{cap,0} + \beta_{cap,1} \left(\frac{DCR - 70}{20} \right) + \beta_{cap,2} \left(\frac{RT_{SOC_{max}} - 127.5}{112.5} \right) + \beta_{cap,3} \left(\frac{SOC_{min} - 18.5}{18.5} \right) + \beta_{cap,4} \cdot T \quad (12)$$

Based on these models, a corresponding orthogonal characterisation experiment could be designed which only takes 155 hours (6.5 days) to conduct. Orthogonal experiments are designed such that the variances of the parameter estimates for the model, $\text{var}(\beta_i)$, are as small as possible and the parameter estimates are mutually independent [19]. As such, the designed orthogonal experiment results in the essential data to fit the models in Equations 11 and 12 and makes sure that the model predictions are as precise as possible. At the same time, the orthogonality criterion ensures that the data is obtained in a minimum amount of time, therefore keeping the experiment as short as possible. A summary of the significant factors from each experiment and the corresponding R^2 and RMSE of the DC RTE models and the DC discharge capacity models is provided in Tables 3 and 4 respectively.

Commented [OD22]: Considerable adjustments and additions to this section have been made to better explain how the results of the previous experiments ultimately lead to the models in Equations 11 and 12. Moreover, the link between these models and the resulting optimal experiment has been clarified and is discussed in more detail than in the original manuscript.

Table 3. Significant parameters and corresponding R^2 and RMSE of the obtained DC RTE models.

Design	Setup	Significant parameters (included in the models)	R^2	RMSE [–]
A	Singe UET	Charge rate, discharge rate, electrolyte temperature	0.934	0.00679
B D – optimal runs	Series UET	Charge rate, discharge rate, maximum SOC, minimum SOC	0.978	0.00873
B D + I – optimal runs	Series UET	Charge rate, discharge rate, maximum SOC, minimum SOC	0.978	0.00726
C	Single UET	Charge rate, discharge rate, resting time maximum SOC, electrolyte temperature	0.957	0.0146
D	Single UET	Charge rate, discharge rate, resting time maximum SOC, minimum SOC, electrolyte temperature	0.860	0.0190

Table 4. Significant parameters and corresponding R^2 and RMSE of the obtained DC Discharge Capacity models.

Design	Setup	Significant parameters (included in the models)	R^2	RMSE [Wh]
A	Singe UET	Discharge rate, minimum SOC, squared minimum SOC, electrolyte temperature	0.957	256
B D – optimal runs	Series UET	Charge rate, discharge rate, maximum SOC, minimum SOC, squared maximum SOC, squared minimum SOC	0.987	206
B D + I - optimal runs	Series UET	Charge rate, discharge rate, maximum SOC, minimum SOC, squared maximum SOC, squared minimum SOC	0.982	189
C	Single UET	Discharge rate, resting time maximum SOC, electrolyte temperature	0.959	406
D	Single UET	Discharge rate, resting time maximum SOC, minimum SOC, electrolyte temperature	0.980	213

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In order to visualise the quality of the models that are obtained from the optimal characterisation experiment, Figure 10 demonstrates the measured versus the predicted values of the performance parameters on the data of Design D.

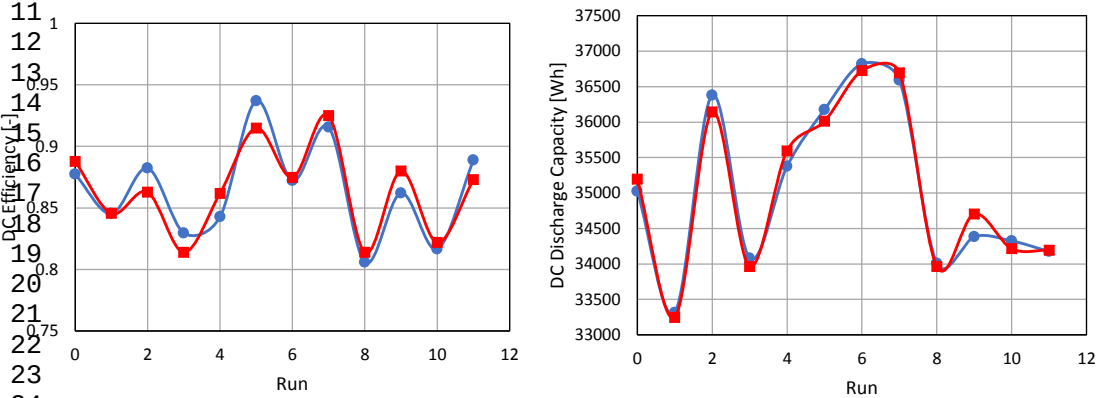


Figure 10. Measured (blue, circles) and predicted (red, squares) values by the models of Equation 11 and 12 on the data of the optimal characterisation experiment D for the DC efficiency (left) and the DC discharge capacity (right).

Reliable models should tell something about the general performance of the battery and should therefore also perform well on the data of other experiments, other than those that provide the data on which they are fitted. The models, fitted on the data from the optimal characterisation experiment, are therefore applied to the data of three previously conducted experiments which follow Design A. They are denoted as A.1, A.2 and A.3. Finally, the models are also tested on the data of an experiment following Design C, which was also conducted on the single RFB setup. Figure 11 displays the measured values of the experiments in blue circles, and the values which were predicted by the model from the optimal characterisation experiment in red squares.

Commented [OD23]: The phrasing was adapted in this paragraph to bring more structure in the results. More explanation is provided as to why it matters that the obtained models provide good predictions on the data of earlier experiments as well.

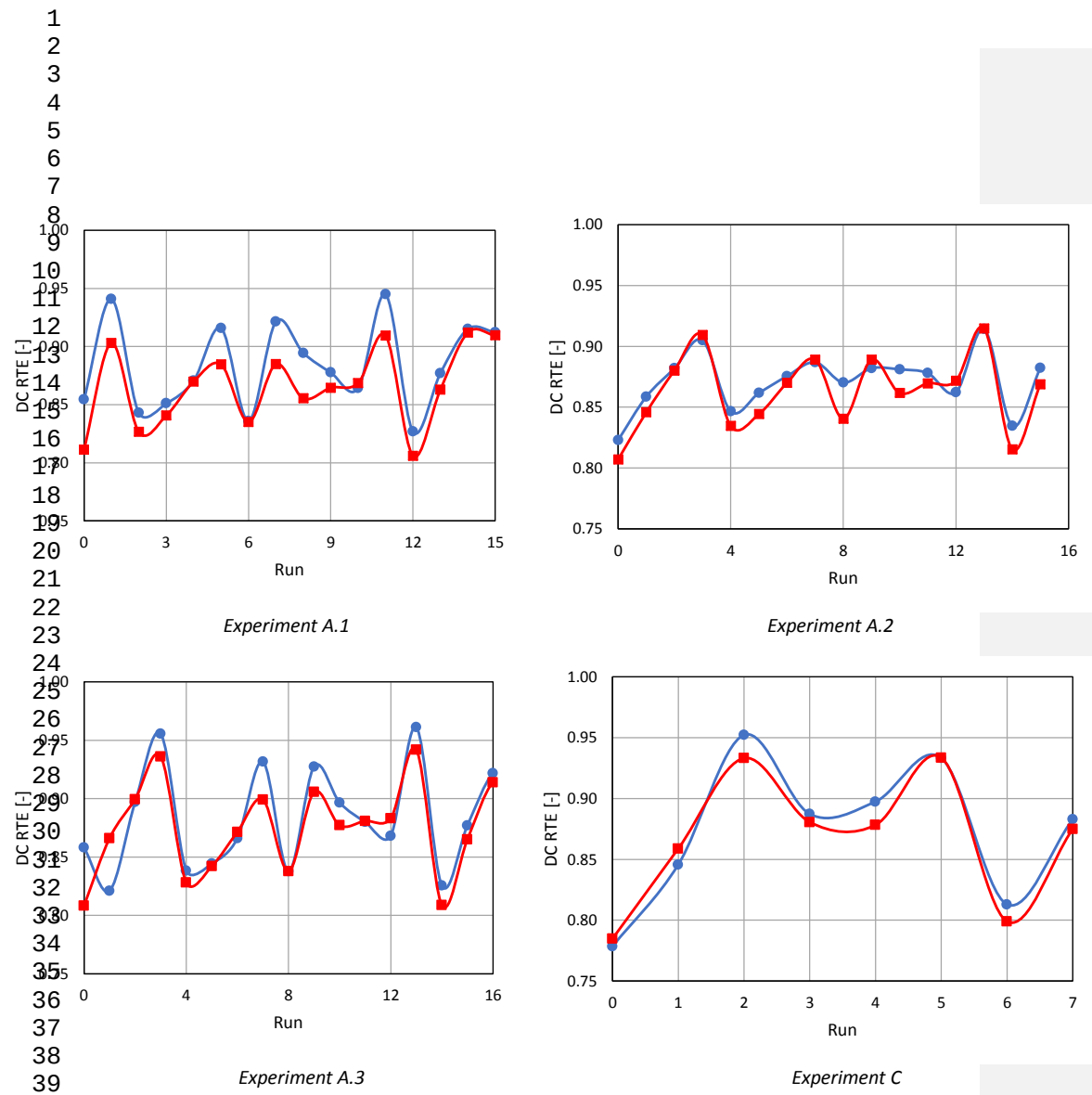


Figure 11. Measured (blue, circles) and predicted (red, squares) values by the DC efficiency model obtained from experiment D, applied to the data of earlier experiments.

Commented [OD24]: The layout of this figure was improved to fit on one page whilst still providing a clear image of the quality of the models.

Likewise, Figure 12 displays the DC discharge capacity model which was fitted on the data from the optimal characterisation experiment. As in Figure 10, the model is applied to the data of three experiments following Design A (denoted as A.1, A.2 and A.3) and one experiment following Design C. The measured values are displayed in blue circles, and the predicted values are displayed in red squares.

Commented [OD25]: This paragraph was extended to provide more clarity regarding the figures.

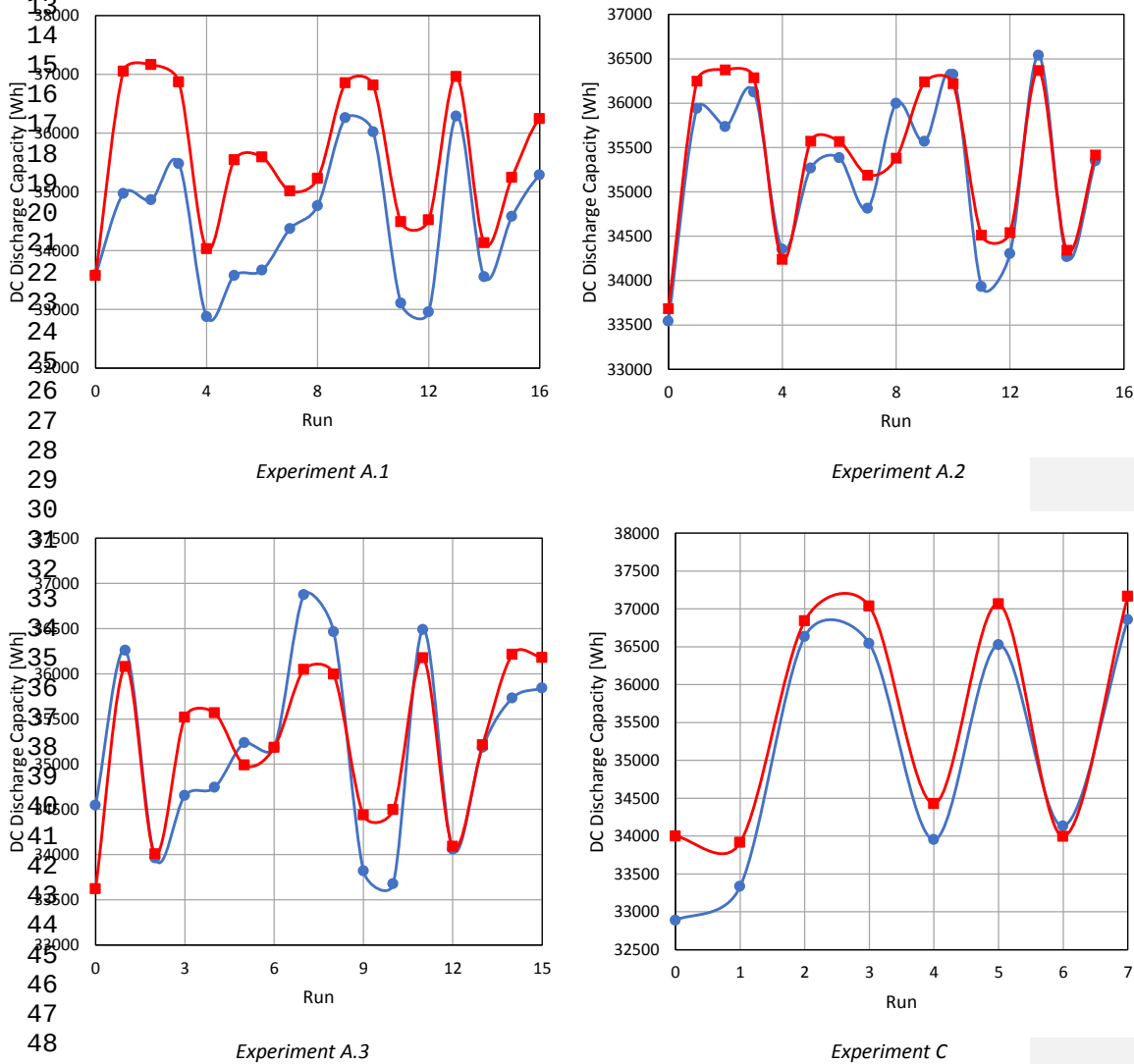


Figure 12. Measured (blue, circles) and predicted (red, squares) values by the DC discharge capacity model obtained from experiment D, applied to the data of earlier experiments.

Commented [OD26]: The layout of this figure was adapted similarly to Figure 11.

These graphs demonstrate that the obtained models can be considered to be generally reliable, which is also expressed through the R^2 and RMSE values of the models on the data of earlier experiments. The statistically designed characterisation experiment therefore considerably outperforms the standard characterisation protocol in the sense that comprehensive and reliable battery performance information can be obtained from an experiment that is significantly shorter.

To indicate how powerful the designed characterisation experiment is compared to the standard protocol, Figure 12 demonstrates that the polynomial models, obtained from Experiment D (which only takes half the amount of time of standard characterisation), can reliably predict the performance of the RFB for the operating points that are classically evaluated during standard characterisation.

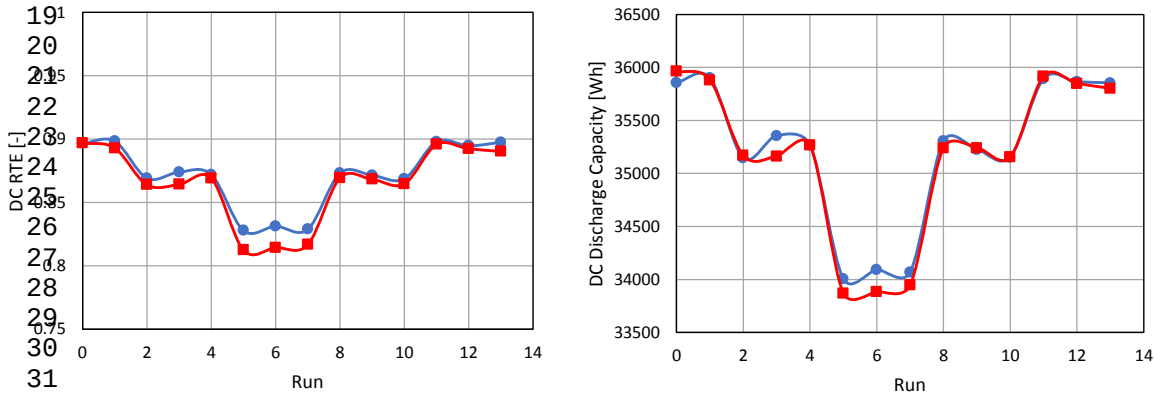


Figure 12 Measured values (blue, circles) of the standard characterisation experiment and predicted values (red, squares) by the polynomial DoE models, obtained from the orthogonal characterisation experiment.

4. Conclusion

Design of experiments has proven to be a reliable and appropriate tool to increase the efficiency and the quality of RFB characterisation experiments. It was shown that battery performance parameters (DC RTE and DC discharge capacity) could be reliably modeled by using only controllable RFB parameters (available to RFB end-users) and the electrolyte temperature. The electrolyte temperature was found to be a highly significant term in the models.

By identifying the parameters which are most influential for the DC RTE and the DC discharge capacity, appropriate RFB performance models could be formulated. This in turn facilitated the design of an optimal characterisation experiment. Identification of the dominant parameters in the system is time consuming but is likely only needed once for every RFB chemistry.

The optimal characterisation experiment results in empirical models for the DC RTE and the DC discharge capacity, which are able to predict RFB performance values for every setting that is within the model ranges. Therefore, the optimised characterisation experiment yields far more useful and comprehensive information than classical characterisation experiments, which only yield performance information for three operating points. Not only does the optimal characterisation experiment yield better information, it also takes a significantly shorter amount of time to conduct. Through DoE, the characterisation time for the 30 kWh UET Reflex module could be reduced from close to 13 days to 6.5 days.

The same principles can be applied to longer duration modules, for which DoE can reduce considerable characterisation times as well. DoE therefore proves its value as an efficient and reliable characterisation tool and considerably outperforms traditional characterisation procedures. As such, the use of DoE can accelerate the implementation and integration of RFBs wherever they can be used.

Commented [OD27]: The conclusion was rewritten. It now better details how we have addressed the challenges laid out in the introduction, and provides clearer information about the significance and the implications of the work.

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Response to Reviewers

We would like to thank the reviewers for the feedback they have provided. The manuscript has been adapted and improved based on your comments.

Reviewer #1: I think it is an interesting work and contains material worth publishing. But there are aspects that need to be improved.

From my point of view, the work presents an experimentation methodology whose main objective is the characterization of redox flow batteries. Unfortunately, the model used for the characterization is not explained in detail and there are things that I do not see clearly.

Response: In the revised article, Section 2.2 is adapted to explain the DoE working method in a clearer and more concise manner. The changes to Figure 4 are discussed in one of the comments below. In the 'Revised manuscript with changes marked', the rewritten paragraphs are marked. After a thorough revision of these paragraphs, the section now better conveys our approach of the models.

In the revised article, Section 2.3 is also rewritten to better explain the parameters and how they play a role in the experiments and the models. Table 1 now provides a clearer overview of the parameters and their properties. As such, it is a valuable addition to the article. In the discussion of the experiments themselves (Section 3), the adapted paragraphs are marked in 'Revised manuscript with changes marked'. In our opinion, the text now better explains how the models are built up in the first place, and how they are adapted based on the results of the experiments.

For example, how is the soc calculated? (is it needed)

Response: The SOC is indirectly measured by comparison with an OCV graph. The studied RFB contains a reference cell through which small amounts of both electrolytes are circulated. The electrolytes remain separated, although not by an active exchange membrane. The OCV of the battery can be measured in this cell at all times. The OCV measurements are automatically compared with the SOC versus OCV curve, which is a one on one relationship provided by the manufacturer. This provides the battery management system with SOC values. This explanation is now added as a footnote to Table 1 as well.

The SOC values are used in this case to study the effect of the minimum SOC and the maximum SOC on battery DC round trip efficiency (RTE) and DC discharge capacity. As such, two SOC-related parameters are studied. As the experiments in Section 3 (Design B, C and D) have demonstrated, these parameters (minimum SOC and maximum SOC) can be used as statistically significant predictors of DC RTE and DC discharge capacity.

In the work it is mentioned that temperature and humidity are variables that will have relevance in the behavior of the battery, but the models do not collect it...

Response: We realise that our discussion of the parameters was not clear in the original manuscript. Therefore Section 2.3 has been thoroughly adapted in the revised article. With the addition of Table 1 in particular, we hope to clarify the parameters better.

In case of the temperature, we make a distinction between the electrolyte temperature and the ambient temperature. Both temperatures are measured and the measurements are processed by the battery management system so the values are readily available. The ambient temperature does not vary significantly during the experiments. This is unsurprising and good for the battery of course, but this also means that this parameter would not contribute to the predictional capabilities of the models. For the same reason, the humidity is not included in the models. The electrolyte temperature on the other hand does vary considerably throughout the experiments. The experiments (Section 3, Designs A and C) show that including this parameter in the models does improve their predictional capabilities.

The argumentation for including the electrolyte temperature in the models is now also clarified in the text. (Section 2.3, below Figure 5)

Specifically for the humidity, we have decided to remove this parameter from the text, as it is of lesser importance in the scope of the article.

Figure 4 is unclear and should be better explained in the text

Response: In the original manuscript, Figure 4 constituted two schematics. In the revised article, this figure is split in two (Figure 4 and Figure 6). Following the revision, Section 2.2 features a clearer explanation of the DoE approach to systems in general, and this system view is visualised in Figure 4. The text of Section 2.2 has been thoroughly adapted to explain the DoE approach more clearly. The explanation is based on the work of Montgomery [1].

As mentioned above, Section 2.3 is expanded with Table 1 and a more elaborate explanation of the parameters and how we use them. As such, we believe that the adapted text of Section 2.2 and 2.3 provides a better framework leading up to Figure 6 (previously part of Figure 4), which visualises the application of the DoE approach to the RFBs.

The authors should make an effort to better organize the work, clarify the objectives and models used.

Response: In the revised article, we made an effort to outline our objectives in a more structured and complete manner. Several paragraphs have been thoroughly adapted to do this and also to clarify our position and the relevance of our research. The paragraphs in the introduction below Figure 1 in particular have been thoroughly revised. The abstract is modified to this aim as well.

Section 3, Design A now features a more elaborate explanation and justification regarding the selection of the starting models. The paragraphs under Design A, p.11 and p.12 have been rewritten in the revised article. Throughout the discussion of the experiments, efforts

are made to better communicate how the results affect the models. Considering the changes to Section 2 as well, we now believe that the objectives and the selection of the models is now explained better.

I also believe that it is necessary to better position the work in the literature.

Response: As our article is the first work to apply DoE to RFB characterisation, the literature that is relevant to the specific scope of our study is rather limited. Nonetheless, we found two additional works that were published in recent months, which can be considered to be relevant in the scope of our article (now denoted as references [16], and [17]). Their relevance to our work is detailed in the introduction, p.3.

Reviewer #2: The revised version are clearer than before, and now the manuscript is acceptable. I have one comment. On Page 12, the authors mentioned that the p-value determines the significance of each parameter. How the p-value is calculated and why the larger than 0.05 is considered non-significant? I would suggest the paper be published after minor revision.

In the revised article, a concise explanation is provided to define the p-value and to explain how it is obtained. The calculation itself is done by calculating the area under the standard normally distributed probability curve. However, this is usually done by the statistical software, JMP in our case.

Regarding the selection of the cut-off p-value of 0.05 to distinguish between significant and insignificant parameters, this is done based on common practice in statistics and is now also mentioned in the text.

Literature mentions that 0.05 is admittedly a rather arbitrary value that has become common practice by frequent use. Different values can be selected depending on the situation. If the cut-off value is selected to be really small, say 0.0005, then the risk for type I errors (false positive) will be really low. This means effects that are not there will rarely be detected. The downside is that small effects will more often be ignored, even if they are active (false negative). Hence, the best cutoff value depends on the implications of type I and type II errors in each specific case [2].

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