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Thesis Changes Log

Name of Candidate: Stanislav Bogdanov
PhD Program: Engineering Systems
Title of Thesis: Modeling and Operation Optimization of Vanadium Redox Flow Batteries
Supervisor: Dr. Mikhail Pugach
Co-supervisors: Associate Professor Federico Martin Ibanez, Skoltech
Dr. Sergei Parsegov, Skoltech

The thesis document includes the following changes in answer to the external review process.

I would like to thank all the jury members for their useful comments and suggestions. After working on them, I made some changes in my thesis, which improves its overall quality. Here are the answers and corresponding thesis changes. For the convenience, the comments of jury members are written in blue, the answers are in black, and the related changes in thesis are in *italic grey.*

Prof. Henni Ouerdane:

1. Avoid writing paragraphs as a single sentence. See, e.g., bottom of page 18.

Thank you for this comment. In the revised version, all single-sentenced paragraphs have been replaced.

2. State clearly the basic scientific hypotheses made to conduct the research.

I highly appreciate this comment. The hypotheses are stated in the section 1.2 of the revised thesis.

The first task is set to find the optimal base model for real-time VRFB simulation, leading to the following hypothesis: a VRFB dynamic model with crossover can simulate VRFB behavior across a wide range of operating parameters (load currents (20 - 300 mA/cm^2) electrolyte flow rates (50 - 300 ml/min) and SOC (10 - 90\%)).

The second task aims to improve the accuracy and applicability of the base model, leading to the following hypothesis: the developed model can simulate the output voltage of the VRFB with RMS error of less than 2\% during 30 charge-discharge cycles.

The third task tests the model's applicability for real test case. As a result, the model should help to develop the optimal operation strategy in the peak shaving problem minimizing its annual operation cost in real power system.

3. Avoid self-praise like in the following sentence found in the Conclusion: "Thus, the results obtained during the thesis research make a great contribution contribution for the development […]". Also note that the word contribution is written twice.

Thank you for this noticing. The self-praises and typos are removed.

4. The statements concerning the further research should be substantiated by some arguments showing not only the interest in the suggested works but also their feasibility. At present, this looks as a wish list.

Thank you for this comment. The paragraph with future directions is rewritten, showing more reasons and details for the research directions:

Since the developed model allows for fast prediction of the VRFB output parameters under various operating conditions, it can be integrated into advanced battery management systems, including digital twins. Therefore, future research can be devoted to the development of such systems based on the presented mathematical model and their implementation in industrial VRFB systems.

In this work, thermal effects were neglected, but in large systems operating over extended periods, these effects can significantly influence VRFB behavior and impose additional requirements on operating modes. Thus, future research should enhance the model to incorporate thermal effects for more precise and informative parameter predictions.

Finally, in Chapter 5, the model was applied to the problem of finding an optimal battery operation strategy in a peak-shaving task for a daily load profile with a single peak. However, in practical applications, this problem requires consideration of additional factors, such as electricity tariffs, integration of renewable sources, and multiple power peaks. Therefore, applying the developed model in a more comprehensive context would be a valuable direction for future studies.

5. Figure captions should systematically end with a full stop

Thank you for this comment. All figure captions are reviewed and revised according to the required format.

6. The title of Chapter 4 could simply read: Comprehensive model for real-time VRFB simulations.

Thank you for this suggestion. Indeed, the title of the chapter 4 can be formulated in simpler manner. It is changed in the revised thesis.

Prof. Aldo Bischi:

1. In the thesis the flow Batteries are often mentioned as important for large scale applications, but in my opinion they are also important for long duration applications not only daily charge-discharge cycles (so Energy/Power ratio above 8-10h), thanks to their modularity, having power and energy decoupled vs Li-Ion where to increase the energy/power ratio you have to oversize them and use it with power lower than the nominal. So it would be interesting to discuss also the long duration and have it considered in the motivation. Sometimes, is mentioned "long-scale" in chapter 2.1, I would improve the clarity. When is discussed in Chapter 3 large and small tank volume, how many h of storage it corresponds? What is meant for industrial application, we are around 5-10kW of power, so it not a matter of size. I would clarify what is meant

I highly appreciate this comment. Indeed, VRFBs have an advantage over other battery types in duration of use. In my thesis, I mentioned many times about the large applications of VRFB. By this term I mean not only higher power and capacity, but also the duration of use. Because in reality, when installing large systems in any application, the longest possible life of the battery is intended.

In the revised version, this point is described in more detail:

The all-vanadium redox flow batteries have reached the most commercialized and developed level, overcoming issues such as cross-contamination and enhancing safety. Initially developed by the Skyllas-Kazacos, VRFBs have evolved from initial lab-scale setups to commercial large-scale systems such as the 4 MW/6 MWh VRFB system in Hokkaido, Japan, and the 200 MW/800 MWh VRFB in Dalian, China. Today, these batteries successfully perform grid support functions for a long period of time such as peak shaving, frequency regulation, and supporting renewable generation.

The developed model also proved its applicability for long-life batteries. Chapter 4 shows that its predictive capability reaches 30 cycles without parameter calibration. This means that if we calibrate the parameters with a certain periodicity, we will be able to use the model almost for the entire battery life.

2. On the objectives and novelty, please elaborate better the last point, I understood it only after reading the Chapter 5, because the optimal operation strategy is often intended as an optimal charge discharge policy of the battery via optimization problems often mixed-integer non-linear, which will tell accordingly to load, renewables production and costs the optimal policy of charge-discharge. The same at point 4 page 39, there are optimization models that take into account the loss of capacity and degradation and accordingly suggest optimal scheduling also of the rebalancing and servicing, see K. Rodby and M. Jafari from MIT (USA) and D. Cremoncini University of Pisa (Italy). While in this work, you decide the scheduling a priori assuming a daily charge discharge cycle, and accordingly the battery is sized and operated optimally to reduce the losses

Thank you for your comment and detailed explanation of this issue. After studying your article, I realized that the term *optimal operation strategy* in my thesis is indeed not used in the same sense as in your article. Therefore, I have changed it to *optimal charging and sizing strategy* in the novelty section:

For the first time, the VRFB model was applied to determine the optimal battery charging and sizing strategy for grid load leveling. This strategy development was based on minimizing the rate of VRFB capacity loss and optimizing the electrolyte volume.

It should also be noted that I used a single daily profile, repeated over many days to simulate battery behavior over one year. I agree that this approach is simplified; however, the goal was to apply the developed dynamic model to the application task. Considering more detailed load profiles is a goal for future research.

3. On Page 79 non isothermal effects are labelled as negligible, please reference it. Then why they should be object of future studies, please elaborate more.

Thank you for this comment. Indeed, it is written that we neglect thermal effects. In my thesis this is done because the temperature of the electrolyte and stack was kept almost constant at room temperature in all experiments. This explanation is also added to the revised thesis:

We also note that in the analysis of the models, we neglected non-isothermal effects because the temperature of the electrolyte and stack was kept almost constant at room temperature in all experiments.

However, these effects should be considered when the large battery is used for long periods at high load currents, because they can lead to additional ohmic losses and capacity losses. From the modeling point of view, taking temperature effects into account complicates the model by addition of a number of parameters, and some of which need to be identified. Therefore, one of the directions of our future research is to develop a non-isothermal model based on the model developed in this thesis to predict voltage and power more accurately, as well as to obtain additional information on temperature behavior.

4. Among the battery's configuration, all the innovative chemistries such organic and the hybrid (with Hydrogen) flow batteries are not considered, is it because we look only at the commercially mature?

Thank you for this comment. We have indeed focused on vanadium batteries because they are the most studied and commercially developed. Their properties are clear and easy to implement in a model.
However, the cost of vanadium flow battery components is quite high, so new flow battery chemistries are being actively developed in research. And the most promising candidates for next gen batteries are organic and hybrid. I believe that these types of batteries will compete with VRFBs in future, but at the moment, the existing systems have drawbacks of low solubility and low cell voltage.

5. This also then for Table 2.1, where to the best of my knowledge the roundtrip efficiency for redox flow batteries above 70% would be then too high, I have seen also at page 25 even 90% is claimed, this is if you look at the cell and not at the whole system. Same other claims of 80-87% not clear if roundtrip or only charge or discharge.

Thank you for this comment. According to the data from different sources, the round-trip efficiency of VRFB can vary from 60 to 85%. See A.A. Kebede, T. Kalogiannis, J. Van Mierlo, M. Berecibar (2022) https://doi.org/10.1016/J.RSER.2022.112213. However, there was a typo on page 25, and I have corrected it here to 85 percent. It was referring to the round-trip efficiency, the charge and discharge.

6. Also for the statement about pumps and shunt currents, being negligible, actually they could easily be shunt of several % points and Pumps/hydraulic losses as well, in the charge and then in the discharge affecting in the roundtrip estimation (e.g. Trovò from Padova University: https://doi.org/10.1016/j.jpowsour.2019.227144). These losses may also be an issue with respect to the scalability, e.g. small pumps and electric motors much less efficient than large ones.

I highly appreciate this comment. Regarding shunt currents, all the considered experimental setups had flow frames with long channels, which minimizes shunt currents. Hydraulic losses were also not considered due to the low viscosity of the electrolyte. However, you are quite right that this can be an issue for certain cases. Introducing these aspects into the model will require sacrificing computation time, which may be critical for real-time applications. However, the model is flexible enough to incorporate shunt currents and hydraulic losses where necessary.

7. In addition, I would encourage to define roundtrip efficiency, state of charge and state of health accurately to avoid misunderstandings.

Thank you for this comment. The round-trip efficiency and state of charge are defined in the page 24:

Before comparison, let us introduce the following terms:

Round-trip efficiency - ratio of the total energy output by the system to the total energy input to the system

State of charge (SOC) - ratio of the remaining charge in the battery, divided by the maximum charge that can be delivered by the battery.

A term “state of health” was not used in the thesis; therefore, it is not necessary to define it.

8. At chapter 5, what would happen if also renewables are considered in addition to the demand profile, an option is filling the battery depending on when renewable are available when electricity is not needed, so that you refill it almost for free because injecting in the grid is not much paid. Actually, here the battery is filled after the sunset (Fig. 5.3), thus not clear why the battery is charged during the load peak when electricity is needed by the user (to reduce the idle time, but is there a concrete need to shift load from 8pm to midnight?

I highly appreciate this comment. It’s true that batteries are often used alongside renewable energy sources. However, incorporating renewable sources into the problem could be addressed as a separate research question. If we were to implement a specific renewable generation profile, then, at times, the battery could indeed be charged almost for free. For modeling purposes, it will be possible to consider both an isolated grid and the integration of renewable sources within the overall grid. These are areas for future research.

Regarding battery charging time, the strategy is as follows: first, the battery is discharged to handle the load peak, then it remains in standby mode at minimal SOC for a period, and afterward, it is charged. The charging start time is selected so that the process finishes just before the next peak, which minimizes capacity losses, as the standby period is primarily at minimal SOC. Charging immediately after discharge would mean the standby period occurs at maximum SOC, which increases capacity losses.

9. About the economic figures please remember to specify the exchange rate adopted, and I was wondering whether you thought at its impact in countries where the cost of electricity is higher, furthermore with 0.05$/kWh one can hardly pay back the cost of the battery itself.

Thank you for this comment. The exchange rate is added in the revised thesis:

With the average cost of electricity in Russia at 0.05 $/kWh (exchange rate is 95 rub per 1 $)

Yes, the average cost of electricity in Russia is quite cheap compared to other countries, but the average value was used in this work to maintain the generality of the methodology. Developing this issue, it is worth considering those regions where the use of flow batteries for the task of peak-shaving would be really profitable. Future studies could be devoted to the consideration of test cases for specific regions or countries, where such details as the cost of materials, electricity, logistics, climate and load profiles could be taken into account.

10. Finally, I would try to stress more on the importance of the model, seeing what are the savings obtained with the charging strategy developed with the model and what one can do without it, to show the economic impact that such detailed model can bring.

Thank you for this comment. Indeed, our model allows for conducting a more detailed analysis showing the benefit of using the optimal charging strategy under different conditions.
I refined this part by simulating the annual operation cost of the VRFB at different load currents, and the results showed that charging with a lower current saves up to 20 % cost at the optimal volume (see Figure 5-7).

I would also like to note, that first and foremost, my work shows the methodology of using a detailed battery model as applied to real test cases and economic studies. More detailed work on the application of this model is the focus of our future research.

11. Pages 34, in "all the above models" not clear to which is referred and which are the "ranges of applicability" mentioned.

Thank you for this comment. I clarify this point in the revised thesis:

It should be noted that Coulomb counter, simple mass-balance approach and advanced mass-balance approach represent the basis for VRFB modeling used in practical applications.

12. The paragraph 2.3.4 Parameters identification, could you guide a bit more the reader introducing to it.

Thank you for this comment. Introductory sentences are added in the revised thesis:

Parameter identification algorithms are mathematical approaches to finding values of uncertain model parameters. They are used to improve the accuracy and predictive capability of the model and, in some cases, help determine the degree of degradation of key battery components.

13. Often used lumped references, I would in general reduce its usage detailing which information each of them brings.

Thank you for this suggestion. I have removed undescribed references in the revised version of the thesis.

14. Sometimes more technical-quantitative terms could be used, e.g. page 30 "complicated models".

Thank you for this comment. I have reviewed the thesis on unclear definitions, and changed it by more clear terms.

15. Sometimes less emphasis, e.g. page 116, "VRFBs emerge as the most promising", it is not a conclusion of this work and I would keep it among the most promising.

Thank you for this comment. It is changed in the following way:
Among various Energy Storage Systems (ESS), vanadium redox flow batteries (VRFBs) emerge as one of the most promising technologies for large-scale stationary applications due to their long lifespan, capability for deep discharge, and relatively low maintenance costs.

16. Some typos, e.g. page 22 "which ensures which ensures".

Thank you for this noticing. The typo is corrected.

Prof. Sun Chuanyu:

1. Page 18, 'This structure provides several advantages: a very long lifecycle of up to 20,000 cycles, flexible scalability, and a high depth of discharge.' I consider the lifespan by years should also be given. For example, 15-20 years.

Thank you for this comment. Indeed, the lifespan in years will be more understandable for general reader. It is added in the revised thesis:
This structure provides several advantages: a very long lifecycle of up to 20,000 cycles (20 --30 years)

2. Page 23, Table 2.1, 'Low energy density and high cost' for RFB may not be accurate. For example, iron-chromium and all-iron RFB are quite cheap, and the high cost is more commonly for VRFB. And for the low energy density, it has been reported that zinc–Iodine hybrid flow batteries possess an

exceptional energy density based on the solubility of zinc iodide (up to 5 M or 167 Wh L −1). So low energy density is more suitable for VRFB as the disadvantage, not all RFBs

Thank you for this noticing. Indeed, properties of RFBs can differ depending on chemistries used. I have corrected this point in the Table 2.1.

3. Page 42, ‘The membrane in the cell serves as a separator of the different electrolytes, while conducting the protons to close the electrical circuit and ensure the continuous flow of the current.’ I consider the membrane can only ensure the transportation of protons, not flow of the current. The current flow should be realized in the metallic cable/wires in the external circuit, not the membrane inside the VRFB system. The descriptions should be modified to be more accurate and reasonable.

Thank for this comment and explanation. Indeed, the current is a flow of the electrons which is realized in the external wires and current collectors, while the membrane passes the protons to keep the electroneutrality of the cell.

The description of the membrane is modified in the revised version of the thesis:

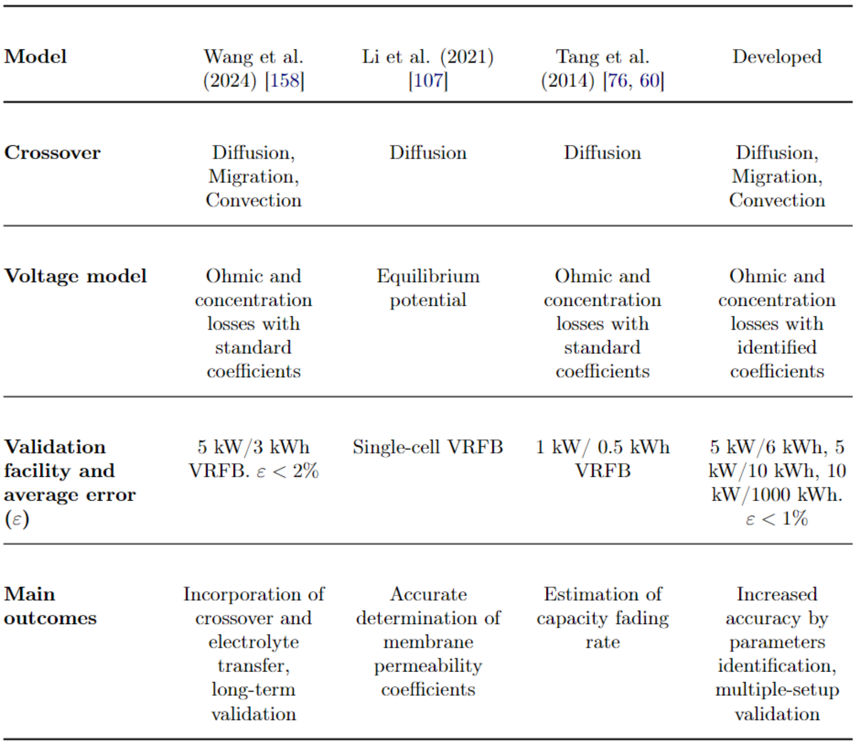
The membrane in the cell serves as a separator of the different electrolytes, while conducting the protons keeping the electroneutrality of the cell.

4. At present, there are many works on modeling of all-vanadium liquid flow battery (VRFB). The model and indicators proposed in this paper should be compared with the key indicators of the model reported in the literature to highlight the superiority of the proposed new model. At present, the main text and chapters seem to mainly describe the results of applying the model to VRFB systems of different power levels, but lack comparison with the indicators in the existing literature. Therefore, it is recommended to further supplement and improve this part.

I appreciate this comment. Indeed, there are number of key studies on real-time modeling reported in the literature. In the revised version, I add the comparison of my developed model with some similar models, which also were validated and applied for real-time simulations:

Finally, the developed model is compared with recent models presented in the literature, which are also applicable for real-time simulation and have been validated against experimental data (see Table 4.8). All models use an eighth-dimensional dynamic model to calculate vanadium ion concentrations and voltage models to determine the output battery voltage. Each model has its own key outcomes; however, the model developed in this thesis stands out in terms of increased accuracy due to the parameter identification algorithm and the quality of validation.

Table 4.8: Comparison of the developed model with existing models



Model	Wang et al. (2024) [158]	Li et al. (2021) [107]	Tang et al. (2014) [76, 60]	Developed
Crossover	Diffusion, Migration, Convection	Diffusion	Diffusion	Diffusion, Migration, Convection
Voltage model	Ohmic and concentration losses with standard coefficients	Equilibrium potential	Ohmic and concentration losses with standard coefficients	Ohmic and concentration losses with identified coefficients
Validation facility and average error (ε)	5 kW/3 kWh VRFB. $\varepsilon < 2\%$	Single-cell VRFB	1 kW/ 0.5 kWh VRFB	5 kW/6 kWh, 5 kW/10 kWh, 10 kW/1000 kWh. $\varepsilon < 1\%$
Main outcomes	Incorporation of crossover and electrolyte transfer, long-term validation	Accurate determination of membrane permeability coefficients	Estimation of capacity fading rate	Increased accuracy by parameters identification, multiple-setup validation

5. The contents in Chapter 5 are a bit short in terms of the length of the chapter. Moreover, the investigation contents in this part should be further enriched. Now compared to other two chapters, this part is quite simple and the conclusions obtained is also quite basic.

Thank you for this comment. Indeed, Chapter 5 is shorter in content than the other chapters. But this chapter proposes an important methodology for using the model in real network peak cutting problems.
Not many input conditions have been considered, but the results already provide insight into the conditions under which it is more profitable and efficient to operate the battery.

Consideration of more detailed conditions, including different load profiles, climate profiles, and electricity tariffs is one of the priority goals for our future research.

Prof. Elena Gryazina:

1. In Fig. 5-1 the units for vertical axes should be in kW not in kWh.

Thank you for this comment. The units in Fig. 5-1 are corrected.

2. The model could benefit from additional validation on larger industrial-scale VRFB systems, which would enhance its credibility for real-world industrial applications.

Thank you for this comment. Indeed, there are projects with MW-scale flow batteries in the world and the developed model could be validated on these systems. However, the thesis presents validation on 3 different industrial-scale systems with powers and capacities of 5 kW/6 kWh, 5 kW/10 kWh and 10 kW/100 kWh, which are already large. To my best knowledge, there is no reported studies with such a detailed validation on kilowatt-scale systems.
Speaking of even larger systems (more than 1 MW), they often have a modular structure with several smaller batteries with a power of several kilowatts connected with each other by wires. Therefore, it can be assumed that if our model works on installations up to 10 kW, which is similar to the module size of a large systems, the validation results can be scaled to a MW-scale VRFB system with preserving the modeling accuracy.

3. The thesis could be improved by offering more specific guidelines for industries aiming to implement the proposed models in practical VRFB systems, particularly regarding the cost-effectiveness of electrolyte rebalancing procedures

Thank you for this comment. Indeed, the cost-effectiveness of the rebalancing procedure is not enough described, so I have added a detailed description in the revised version:

The cost of this procedure consists of the cost of the additional electricity required to recharge the battery, the cost of the necessary equipment to mix the electrolytes, and the cost of labor. These costs are calculated in more detail in Section 5.4.2. Regarding the timing of this procedure, it takes several hours, so it can be performed during standby periods when the battery is not operated in the grid.

Regarding general guidelines to industries, they can vary quite a bit depending on the task performed, battery size and installed equipment. Therefore, my thesis specifies a general modeling methodology and examples of applications to test cases.

Dr. Dmitry Titov:

1. It was noted that most previously developed VRFB models were applied to small-scale setups and are not suitable for large-scale systems. However, what is the actual difference between small and large setups in terms of modeling? Since the battery design remains the same regardless of scale, it seems the model parameters could simply be scaled and applied to larger systems. More clarity is needed on the specific challenges or requirements for modeling large-scale systems.

Thank you for this comment. Indeed, the transition from small-scale systems to industrial-scale system is not very clear. In the section 4.1 of the revised version, I have modified the explanation of this point:

Previously, we have considered modeling of lab-scale VRFB systems. Larger industrial-scale VRFBs use a larger number of cells in stack, a larger volume of electrolyte, and a larger active area of electrodes in each cell. The VRFB performance depends on the state of its key components (i.e. membrane, electrodes and electrolyte). During long battery cycling, the components inevitably degrade, leading to the battery capacity fading and the decrease of efficiency. Experimental results have shown that the specific resistance of the cell exhibits a nonlinear dependence on the state of charge and can vary with current. Additionally, the technical parameters of the membrane may change over time and with operating conditions due to the different contributions of crossover mechanisms. Electrolyte degradation leads to a loss of available battery capacity, which can significantly alter battery voltage and complicate the control and monitoring process of VRFBs. Therefore, to ensure the proper prediction of VRFB behavior, it is necessary to detect these changes in key parameters and adjust the model accordingly.

Disconnecting and disassembling the battery stack in order to repeatedly measure the model parameters is a long and unprofitable process. Therefore, an additional requirement for modeling an industrial-stack battery is to adjust the model parameters to the current degradation of the main battery parts in real-time without battery disconnecting.

One approach to parameter adjustment is measuring them with additional equipment. However, in industrial systems, the design may not allow for the installation of extra equipment. Furthermore, additional measurements often require stopping the battery's operation and disassembling it, which may be impractical in industrial settings. Thus, an effective method for parameter adjustment is their identification through the approximation of experimental curves. This method enhances model accuracy in real-time without relying on external measurements. This chapter develops a new model that includes a parameter identification algorithm. The algorithm is verified for typical cases of battery degradation and applied to determine the current state of three different large-scale installations.

2. The developed model does not account for shunt currents; however, their impact is noticeable in large stacks. How does this omission affect the accuracy of the model?

Thank you for this comment. Indeed, the impact of shunt currents can be noticeable in case of a large number of cells in the stack and small channels electrical resistance. However, in my work, all the considered experimental setups had flow frames with long channels, which increases their electrical resistance and minimizes shunt currents. Therefore, the share of shunt-current losses was no more than 2 % in the total battery losses. This explanation is also added to the revised thesis (p.85):

It also should be noted that shunt currents are neglected in this study due to their small impact on the battery voltage due to the large electrical resistance of the channels in the cell.

3. In Section 3.3, activation voltage losses are introduced, but they are neglected in the simulations. This inconsistency could be confusing. The author should clarify the rationale for omitting activation losses in the simulations.

Thank you for this comment. Activation overpotential is usually small in comparison with ohmic and concentration overpotentials due to the use of porous electrodes with high surface area, which minimizes current densities. Therefore, activation overpotential can be combined with ohmic losses by introducing the equivalent cell resistance. This is also added to the revised thesis:

In experimental systems, activation overpotential is usually small in comparison with ohmic and concentration overpotentials due to the use of porous electrodes with high surface area, which minimizes current densities. Therefore, activation overpotential can be combined with ohmic losses by introducing the equivalent cell resistance R_{el}^{*}*:*

$$I\,R_{el}^{*} = U_{ohm} + U_{act}$$