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# Thesis Changes Log

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**PhD Program:** Engineering Systems

**Title of Thesis:** Vanadium Redox Flow Batteries modeling and performance analysis

**Supervisor:** Assistant Professor Aldo Bischi

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

I would like to express my gratitude to reviewers for the invaluable comments and the opportunity to respond to them. Please find below my response together with improvements and enhancements included in the revised revision.

1. In the literature overview it is highly desirable to have a part discussing the advantageous and shortcomings of vanadium redox flow batteries over other redox flow batteries. No other types of such systems are described such that after reading Chapter 2 the vanadium-based technology is clearly perceived as the only and absolute one with no alternatives in the field. The candidate is kindly recommended to add some information on other types of redox flow batteries. Also, more comparison is expected with commercialized Na-S batteries and emerging Na/K-ion ones that are also primarily aimed at grid energy storage.

   - In the revised version the advantages and limitations of NaS batteries (see p. 41 – 42) as well as other types of flow batteries (see p. 47 – 48) are introduced and compared with VRFB.

2. The crossover modelling does not take into account the material type and porosity of the membrane which can be detrimental. Please add some explanation why those are neglected.

   - The properties of membrane as are taken into account for simulation of crossover flux (see Eq. (15) – (17)).

3. What is the standard electrochemical potential of the redox reaction occuring in VRFB? A crucial characteristic that is not given in the thesis.

   - In the revised version the standard electrochemical potential of vanadium redox couples has been added (see p. 52).

4. There is a mistake in labeling curves in Fig. 20; “Q3, Q2, Q3”. Q1 is missing.

   - Thanks for this comment. In the revised version the misprint is fixed.

5. A question related to the experimental part: the Nafion membrane was pre-treated by boiling in H2O2 and H2SO4 or just keeping in the solution of them? Boiling in H2O2 does not make much sense due to the decomposition of the latter.

   - This is the standard procedure for pre-treatment of Nafoin membrane. Please see [1].

     [1] B. Jiang, L. Yu, L. Wu, D. Mu, L. Liu, J. Xi, X. Qiu, Insights into the Impact of the Nafion Membrane Pretreatment Process on Vanadium Flow Battery Performance, ACS Appl. Mater. Interfaces. (2016). https://doi.org/10.1021/acsami.6b03529.

6. Considering the size and impact of the field of VRFB the reviewer expected to see more references in the reference list than 117 (some of them being direct links to webpages, not refereed work). Including the response to the first comment might possibly help addressing this issue as well and increase the number of papers crucial for RFB and related fields.

   - In the revised more references have been added.

7. On page 95 in the Eq. 33 gamma (γ) is written instead of beta (β). Please, check.

   - Thank you for this comment. In the revised version the misprint has been fixed.

8. Section 2.2 is poor in references, as there are many types ESS. It will be good to have at least one reference of each technology.

   - In the revised more references have been added.

9. In pag. 34, FC means fuel cell right? Try to avoid acronims if there are not really necessary.

   - In the revised version it was removed.

10. In Section 2.3 could you please clarify what is smoothing instability?

    - In the revised version more explanation has been added (see p. 35).

11. In pag. 38, CAES and PHS have a short response time or a slow response?

    - Thank you for this comment. In the revised it was changed to slow response.

12. In pag. 38, what is the relation with the toxicity of the batteries and the first and second boundaries?

    - The toxicity of the batteries has not been discussed here, as the boundaries are derived from the main technical indicators of storage systems, related to their response time, scalability and cost of power and energy units.

13. Pag. 47, try to be accurate “several V” sounds too vague.

    - Thank you for this comment. In the revised it was changed to “1.5 V”.

14. Pag. 50, eq. number please put it in the correct place.

    - Thank you for this comment. In the revised it was changed.

15. Fig. 15, PCS is what? Avoid acronyms when is possible

    - PCS is a power conditioning system that includes inverter, converter and battery management system. This information is shown in the fig. caption (see p. 55).

16. In pag. 57, empirical models , could you add some references?

    - The references have been added (p. 59).

17. Pag. 60, technics or techniques? Tool or tools?

    - Thanks for this comment. In the revised version the misprints are fixed.

18. Pag. 60 When the first numerical dynamic zero model was developd? Add please some dates. Also in pag. 61, it will be good to know the progress chronologically

    - In the revised version the key dates have been added (see p.62 - 63).

19. Eq. (4) please explain +/- signs, in general equations are not well explained and detailed try to be explain the concepts clear.

    - In the revised version the explanation has been added.

20. Pag. 65, in general I would avoid the term “a bit” for example you can say slightly smaller…
    - In the revised it was changed.

21. Pag. 65, the model is difficult to follow as the variables are not mentioned in the text only in the glossary, an analysis of each term can be useful. Also eq (15) – (17)

    - In the revised version the description of the variables has been added.

22. Pag. 68, you can explain what is lambda.
    Pag. 68 please mention what is Ved
    - In the revised version the description of the variables has been added.

23. Pag. 70, probably if you give some range for alpha and beta it will help and some values for Ilim

    - In the revised version the ranges have been added (see p. 73).

24. Pag. 71 you define SOC, but it was mentioned before

    - In the revised version it has been fixed.

25. Pag. 72 typo error They can also….

    - Thank you for this comment. In the revised version it has been fixed.

26. In Section 3.7, experimental results, I miss some pictures of the test bench

    - In the revised version the photo of the teat bench has been added (see Fig.19, p. 80).

27. Fig. 29, Q3, Q2, Q1 are not clear

    - Thank you for this comment. In the revised version it has been fixed.

28. Pag. 80 typo witch

    - Thank you for this comment. In the revised version it has been fixed.

29. In (33) it is beta or gamma, the text talks about beta and in (33) is gamma

    - Thank you for this comment. In the revised version it has been fixed.

30. I would appreaciate a better explanation about Fig. 26.

    - In the revised version the figure has been changed by highlighting the connection of the approaches through a common box with interpolated efficiencies.

31. Last paragraph of 99 is confusing, where re the cycles?

    - In the revised version it has been removed.

32. In (34) j is what? Current? Or the number of cell? It is confusing

    - j is the current density, while $n_{ce}$ is the number of the cells.

33. Pag. 100 is important for understanding the crossover effect. It will be good if you can clarify the concepts using figures.

    - Looks like there is a wrong page number, as the crossover was not mentioned on p.100. Nevertheless, the crossover has been analyzed in the Chapter 3 while here we were focused on its effect on the capacity drop that was investigated in details further in this Chapter (see p. 113 – 114 of the revised version).

34. The coulobic efficiency is around 88% and 70%) for VRFB what is in other technologies?

    - Actually, what we call here the "coulombic efficiency" is related to electrolyte utilization that shows how much of the total theoretical capacity is used in charge or discharge process. The coulombic efficiency in the classical meaning is shown in Fig. 24 and can be compared with the one of Li-ion batteries.

35. It seems like Pag. 115 was written before

    - In the revised version it has been fixed.

36. First paragraph pag. 117 is not clear.

    - The standard approach is described in Sec. 4.5. Here we explained that we compared three different approaches (standard, our, and numerical simulations) using the numerical simulation results as a reference.

37. Acronyms NS PR and ST can be avoided

    - It is quiet complicated as in this case they need to be fully written in the graph legends that will take a lot of place.

38. Fig. 40 Can you normalize the curves somehow?

    - If we normalize the curves, then the figure will be less representative.

39. Section 4.7, can you explain why the crossover presents an asymmetric behavior?

    - It has been explained in Sec. 4.6.1 "In order to understand the asymmetric behavior of crossover, we need to look at the main driving forces…" (see p. 113-114).

40. Section 5.1, the current is determined by an inverter if the battery is connected to a AC grid using just an inverter. In general it will be the power electronic converter which can be a combination of DC/AC and DC/DC convetters.

    - Thank you for this comment. In the revised version it has been fixed.

41. Section 5.1 probably a is needed to clarifiy the ideas.

    - To better explain the concept, a new figure has been added (see Fig. 41, p.130).

42. Section 5.1 About damping and oscillations in 2nd paragraph, please add some references

    - The representative current drop and the battery response has been shown on a new figure (see Fig. 42, p. 131).

43. Again you mention many control methods, some diargrams will help to understand the differences

    - The main control methods have been represented in a table (see Table 8, p. 134).

44. In pag. 128, why a PI controller requires such a significant computational power?

    - The explanation is presented in the text: “Moreover, the real-time computation of the proposed reference trajectory…” (see p. 133).

45. In pag 140, you define VE and EE but I saw the same efficiency before in the text.

    - Yes, we decided to put it here in order to remind the reader, how they can be calculated.

46. Can you highlight the important numbers in table 9, can you explain it in the text?

    - In the revised version this information has been added (see p. 150).

47. Pag. 151, “our paper” or this thesis?

    - Thank you for this comment. In the revised version it has been fixed.

48. Page 10: Incorrect units of current density. It should be probably A cm?

    - Thank you for this comment. In the revised version it has been fixed.

49. Page 11: Incorrect units of OCV. it should be V (not W).

    - Thank you for this comment. In the revised version it has been fixed.

50. Page 12: voltage averaged over the operation time has the same symbol as power averaged over the operation time
    Page 13: Both channel and charge uses same acronym “ch”

    - Thank you for this comment. In the revised version it has been fixed.

51. Page 33: Hydrogen production via electrolysis should be rather include in a section of electrochemical energy storage.

    - Yes, it can be an option. However, here we were focused on the technologies, that are implemented for big scale energy storage systems and in this case it was included in the chemical section [2].

      [2] M. Aneke, M. Wang, Energy storage technologies and real life applications – A state of the art review, Appl. Energy. 179 (2016) 350–377. https://doi.org/10.1016/j.apenergy.2016.06.097.

52. Page 34 : Remark : The flow system with liquid or suspension electrolytes can be also categorised as fuel cells , when operating in discharge mode only.

    - Yes, thanks.

53. Page 47 : The term "Proton exchange membrane " (PEM ) is usually used in hydrogen - oxygen fuel cells and water electrolysis . In RFB term “Cation exchange membrane " (CEM) is more appropriate as the electrolytes contains typically several cations which can permeate across the membrane .

    - Thank you for this comment. In the revised version it has been fixed.

54. Page 50 : Arrow "↔" is not suitable for the use in electrochemical reactions (it is typically used to express resonance equilibria in organic chemistry ) and it should be replaced by " $\rightleftharpoons$ " .

    - Thank you for this comment. In the revised version it has been fixed.

55. Page 50 : It is not correct to use V5 + and V4+, as the corresponding ions are $VO_2^+$ and $VO^{2+}$ .

    - Thank you for this comment. In the revised version it has been fixed (see p.52).

56. Page 52 : Energy density of VRFB ( 1st generation electrolyte ) is only 15-25 Wh/ L.

    - Thank you for this comment. In the revised version it has been fixed.

57. Page 76 : Was the substance amount of vanadium in the negative electrolyte really double when compared to the positive one ? (20 ml of 1.0 M VOSO4 for positive and 20 ml of 1.0 M V2 (SO4 )3)

    - Thank you for this comment. In the revised version it has been fixed.

58. Page 78 : For direct comparison between various cells it is more useful to present cell resistances in the form of are specific resistance , i.e. , multiplied by the geometric area of the active zone . In this case, that would be 0.65 Ohm $cm^2$.

- Thank you for this comment. Yes, it is correct, in the revised version it has been fixed.

59. Page 95: Equation 32 is not correct as all the cells contribute to the total battery resistance equally in serial connection of the cells in the stack. It is true that the neighboring cells share common bipolar plate, but the contribution of bipolar plate on the cell resistance is usually almost negligible.

- Thank you for this comment. In the revised version it has been fixed. Nevertheless, it is not significantly affect energy losses analysis, as it does not change the observed trends.

60. Moreover, I have one more questions regarding the developed stack model : In the chapter 4 the single -cell model, described in chapter 3, is extended for the stack simulation , but the effect of shunt currents is neglected. Is this a reasonable approximation for the stack geometry used for the model validation? What is the expected effect of shunt currents on the battery efficiency and available capacity?

- Yes, the shunt currents have not been considered in the presented stack model due to their small impact during dynamic battery operation [3]. The validation showed good agreement with experimental data. We assume, that the presented data had been obtained for the stack geometry with minimized shunt current losses, even though the authors did not specify it explicitly [4].

[3] A. Tang, J. McCann, J. Bao, M. Skyllas-Kazacos, Investigation of the effect of shunt current on battery efficiency and stack temperature in vanadium redox flow battery, J. Power Sources. 242 (2013) 349–356. https://doi.org/10.1016/j.jpowsour.2013.05.079.

[4] P. Zhao, H. Zhang, H. Zhou, J. Chen, S. Gao, B. Yi, Characteristics and performance of 10kW class all-vanadium redox-flow battery stack, J. Power Sources. 162 (2006) 1416–1420. https://doi.org/10.1016/j.jpowsour.2006.08.016.